the rotations, which are marked by torsion angle C(3)—C(8)—C(9)—C(14) and the corresponding angle C(5)—C(7)—C(15)—C(20) [12·9 (3) and 12·4 (3)° for (I), 31·5 (9) and 26·1 (10)° for (II)]. The benzylidene planes of (I) are less tilted from *A* than those of (II). In addition, (I) shows more stereosymmetry than (II) in overall geometry. The replacement of an N(1) proton of (I) by a methyl group to give (II) changes the piperidone ring from a boat to a chair conformation and changes some of the torsion angles of the aryl groups. The differences in shape between (I) and (II) may account, in part at least, for the marked disparity in cytotoxicity between the two compounds.

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Structures of *N,N,N′,N′*-Tetramethylbenzidine (I) and 4,4′-Methylenebis(*N,N*-dimethylaniline) (II)

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Abstract. (I) $C_{16}H_{20}N_2$, $M_r = 240·35$, orthorhombic, $Pna2_1$, $a = 11·445$ (2), $b = 15·598$ (3), $c = 7·588$ (1) Å, $V = 1354·6$ (4) Å^3, $Z = 4$, $D_x = 1·178$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 0·54 mm^{-1}, $F(000) = 520$, $T = 295$ K, $R = 0·054$ for 1170 observed reflections [$F_o > 2\sigma(F_o)$]. (II) $C_{17}H_{22}N_2$, $M_r = 254·38$, tetragonal, $P4_12_12$, $a = 6·3500$ (3), $c = 36·647$ (3) Å, $V = 1477·7$ (2) Å^3, $Z = 4$, $D_x = 1·143$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 0·52 mm^{-1}, $F(000) = 552$, $T = 295$ K, $R = 0·054$ for 877 observed reflections [$F_o > 3\sigma(F_o)$]. The methylene group in (II) lies on a twofold axis. One of the dimethylamino groups in (I) is planar and the other in (I) and those in (II) adopt approximately planar conformations. The dihedral angle between the two benzene rings in (I) is 13·0 (1)°.

Introduction. As part of an investigation of how substituents affect the conformation of dimethylamino groups in six-membered aromatics, the structures of (I) and (II) were determined by X-ray analysis to compare the conformations with those in 4-*N,N*-dimethylamino-pyridine *N*-oxide dihydrate (III) (Nakai, Saito & Yamakawa, 1988*a*) and *N,N*-dimethyl-1,4-phenylenediamine (IV) (Nakai, Saito & Yamakawa, 1988*b*). The dimethylamino group in (III) adopts a planar conformation, but that in (IV) adopts a pyramidal one in which the N atom is involved in a hydrogen bond. The two phenyl rings in (I) can conjugate with each other, but they cannot in (II) because the central methylene group interferes with the π-electron transfer between the phenyl rings.

Experimental. Rigaku AFC-5R diffractometer, graphite-monochromatized Cu $K\alpha$. Structures solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

(I) Colorless prismatic crystals obtained from an ethyl acetate solution. Crystal of dimensions 0·4 × 0·4 × 0·5 mm, cell dimensions determined from 2θ angles for 25 reflections in the range $26 < 2\theta < 44°$. Intensities measured up to $2\theta = 140°$ in h 0/13, k 0/18 and l 0/8, ω–2θ scans, ω-scan width $(1·2 + 0·2\tan\theta)°$, three standard reflections monitored every 100 measurements showed no significant change. 1315 unique reflections measured, 1170 intensities observed

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[$F_o > 2\sigma(F_o)$, ten very strong reflections rejected], no absorption corrections. H atoms located on a difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by block-diagonal least squares. Temperature factor of each H atom assumed to be equal to B_{eq} of the bonded atom. $\sum(w|\Delta F|^2)$ minimized, $w = 1/[\sigma^2(F_o) + 0{\cdot}0037|F_o|^2]$, $w = 0$ for 14 reflections with $w^{1/2}|\Delta F| \geq 3$. Final $R = 0{\cdot}054$, $wR = 0{\cdot}072$, $S = 1{\cdot}089$. The highest and lowest peaks in the final difference map were 0·3 and −0·2 e Å^{-3}. Max. Δ/σ in the final refinement cycle 0·3. Atomic scattering factors calculated from $\sum[a_i\exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ ($i = 1, \ldots, 4$) (*International Tables for X-ray Crystallography*, 1974). Calculations performed on FACOM M340R computer at Shionogi Research Laboratories.

(II) Colorless plate crystals obtained from an acetone solution. Crystal of dimensions 0·4 × 0·4 × 0·4 mm, cell dimensions from 2θ angles for 25 reflections ($29 < 2\theta < 44°$). Intensities measured up to $2\theta = 140°$ in h 0/7, k 0/5 and l 0/44, ω–2θ scans, ω-scan width $(1{\cdot}2 + 0{\cdot}2\tan\theta)°$, three standard reflections monitored every 100 measurements showed no significant change. 918 unique reflections measured, 877 intensities observed [$F_o > 3\sigma(F_o)$], no absorption corrections. H atoms located on a difference density map. Positional and thermal parameters were refined initially by block-diagonal least squares and finally by full-matrix least squares using *CRYLSQ* (Olthof-Hazekamp, 1987). Anisotropic thermal parameters for C and N, and isotropic for H. $\sum(w|\Delta F|^2)$ minimized, $w = 1/[\sigma^2(F_o) + 0{\cdot}0009|F_o|^2]$, $w = 0$ for three reflections with $w^{1/2}|\Delta F| > 3$. Correction for isotropic secondary extinction (Zachariasen, 1967), extinction coefficient $= 1{\cdot}4\,(1) \times 10^{-3}$, $R = 0{\cdot}054$, $wR = 0{\cdot}072$, $S = 0{\cdot}732$. The highest and lowest peaks in the final difference map were 0·09 and −0·01 e Å^{-3}. Max. Δ/σ in the final refinement cycle 0·2. Atomic scattering factors generated using tables from Cromer & Mann (1968). Calculations performed on VAX 11/780 computer at Shionogi Research Laboratories.

Discussion. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1. Bond lengths and angles are given in Table 2.* Perspective views of the molecules with the atom-labeling systems are shown in Fig. 1. Stereoviews of the crystal packings drawn using the program *PLUTO* (Motherwell & Clegg, 1978) are presented in Fig. 2.

No stackings between molecular planes and no intermolecular contacts shorter than the sum of the van der Waals radii were found in the crystal structures of (I) and (II).

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(I)				
C(1)	0·8731 (1)	0·1288 (1)	0·2887 (3)	3·42 (3)
C(2)	0·9534 (1)	0·0810 (1)	0·1924 (3)	4·06 (4)
C(3)	0·9547 (1)	−0 0080 (1)	0·1924 (3)	4·06 (4)
C(4)	0·8737 (1)	−0·0544 (1)	0·2932 (3)	3·68 (4)
C(5)	0·7919 (1)	−0·0071 (1)	0·3891 (3)	4·20 (4)
C(6)	0·7922 (1)	0·0818 (1)	0·3866 (2)	3·73 (4)
N(7)	0·8762 (1)	−0·1431 (1)	0·2999 (3)	5·02 (4)
C(8)	0·7766 (2)	−0·1903 (1)	0·3596 (4)	5·66 (6)
C(9)	0·9672 (2)	−0·1895 (1)	0·2146 (4)	5·79 (6)
C(10)	0·8744 (1)	0·2242 (1)	0·2902 (2)	3·37 (3)
C(11)	0·7825 (1)	0·2723 (1)	0·3573 (3)	4·62 (5)
C(12)	0·7838 (1)	0·3610 (1)	0·3624 (3)	4·74 (5)
C(13)	0·8783 (1)	0·4076 (1)	0·2956 (3)	3·69 (3)
C(14)	0·9706 (1)	0·3601 (1)	0·2256 (3)	4·35 (4)
C(15)	0·9677 (1)	0·2708 (1)	0·2230 (3)	4·15 (4)
N(16)	0·8799 (1)	0·4962 (1)	0·3004 (3)	5·21 (4)
C(17)	0·9728 (2)	0·5437 (1)	0·2225 (4)	5·64 (6)
C(18)	0·7842 (2)	0·5427 (1)	0·3762 (4)	5·16 (5)
(II)				
C(1)	0·2020 (3)	0·0295 (3)	0·27108 (4)	4·72 (4)
C(2)	0·2837 (3)	−0·1255 (2)	0·29373 (4)	4·73 (4)
C(3)	0·4590 (3)	−0·0898 (3)	0·31524 (4)	4·74 (4)
C(4)	0·5607 (3)	0·1075 (3)	0·31541 (4)	4·50 (4)
C(5)	0·4789 (3)	0·2614 (3)	0·29206 (4)	5·11 (4)
C(6)	0·3052 (3)	0·2217 (3)	0·27067 (4)	5·18 (5)
N(7)	0·7304 (3)	0·1456 (3)	0·33783 (5)	6·42 (5)
C(8)	0·8494 (4)	0·3386 (4)	0·33378 (9)	6·96 (7)
C(9)	0·8261 (5)	−0·0173 (4)	0·35904 (7)	7·00 (6)
C(10)	−0·0009 (3)	0·0009 (3)	0·25	6·29 (6)

Our study shows the non-planarity of the dimethylamino groups by the angle, η, between the C(*ipso*)—N bond and the plane of the three non-hydrogen atoms in the dimethylamino group. The η values are 0·1 (2)° for (III) and 41·7 (2)° for (IV). In (I), $\eta = 10{\cdot}9\,(3)°$ for the N(7) amino group and 2·8 (3)° for the N(16) amino group, while $\eta = 12{\cdot}6\,(3)°$ for (II). The C(*ipso*)—N bond lengths, d_{CN}, in (I) and (II) are close to each other, being longer than 1·351 (2) Å in (III) and shorter than 1·425 (3) and 1·430 (3) Å in (IV). In these compounds, the η values show an approximately linear correlation with d_{CN}; the former decreases as the latter decreases. A decrease of d_{CN} indicates an increase of conjugation interaction between the amino group and the aromatic ring. Therefore, an increase of the conjugation interaction leads to an increase of the planarity of the dimethylamino group or *vice versa*.

In compounds with a substituent strongly interacting with a π conjugation system, such as (III) which includes a strong electron-attracting group and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine which includes a strong electron-releasing group, $\eta = 27\,(1)$ and 28 (1)°, $d_{CN} = 1{\cdot}42\,(1)$ and 1·41 (1) Å, respectively (Ikemoto, 1979), the conformation of the dimethylamino group depends predominantly on the electronic property of the substituent. The other

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* Lists of structure factors, anisotropic temperature factors of the non-H atoms and atomic coordinates of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51237 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(I)

C(1)–C(2)	1·391 (3)	C(10)–C(11)	1·389 (3)
C(1)–C(6)	1·395 (3)	C(10)–C(15)	1·389 (3)
C(1)–C(10)	1·488 (3)	C(11)–C(12)	1·384 (3)
C(2)–C(3)	1·388 (3)	C(12)–C(13)	1·398 (3)
C(3)–C(4)	1·403 (3)	C(13)–C(14)	1·395 (3)
C(4)–C(5)	1·397 (3)	C(13)–N(16)	1·383 (3)
C(4)–N(7)	1·385 (3)	C(14)–C(15)	1·393 (3)
C(5)–C(6)	1·387 (3)	N(16)–C(17)	1·424 (4)
N(7)–C(8)	1·431 (4)	N(16)–C(18)	1·434 (4)
N(7)–C(9)	1·424 (4)		

C(2)–C(1)–C(6)	115·9 (2)	C(1)–C(10)–C(11)	122·4 (2)
C(2)–C(1)–C(10)	122·2 (2)	C(1)–C(10)–C(15)	121·9 (2)
C(6)–C(1)–C(10)	121·9 (2)	C(11)–C(10)–C(15)	115·7 (2)
C(1)–C(2)–C(3)	122·9 (2)	C(10)–C(11)–C(12)	122·8 (2)
C(2)–C(3)–C(4)	120·6 (2)	C(11)–C(12)–C(13)	121·2 (2)
C(3)–C(4)–C(5)	117·0 (2)	C(12)–C(13)–C(14)	116·6 (2)
C(3)–C(4)–N(7)	121·5 (2)	C(12)–C(13)–N(16)	121·4 (2)
C(5)–C(4)–N(7)	121·5 (2)	C(14)–C(13)–N(16)	122·1 (2)
C(4)–C(5)–C(6)	121·3 (2)	C(13)–C(14)–C(15)	121·2 (2)
C(1)–C(6)–C(5)	122·3 (2)	C(10)–C(15)–C(14)	122·4 (2)
C(4)–N(7)–C(8)	120·6 (2)	C(13)–N(16)–C(17)	121·3 (2)
C(4)–N(7)–C(9)	120·4 (2)	C(13)–N(16)–C(18)	120·4 (2)
C(8)–N(7)–C(9)	117·7 (2)	C(17)–N(16)–C(18)	118·3 (2)

(II)

C(1)–C(2)	1·388 (2)	C(4)–C(5)	1·399 (2)
C(1)–C(6)	1·385 (3)	C(4)–N(7)	1·376 (3)
C(1)–C(10)	1·513 (2)	C(5)–C(6)	1·376 (3)
C(2)–C(3)	1·383 (3)	N(7)–C(8)	1·447 (3)
C(3)–C(4)	1·410 (3)	N(7)–C(9)	1·429 (3)

C(2)–C(1)–C(6)	117·0 (2)	C(5)–C(4)–N(7)	122·2 (2)
C(2)–C(1)–C(10)	122·6 (1)	C(4)–C(5)–C(6)	121·2 (2)
C(6)–C(1)–C(10)	120·2 (1)	C(1)–C(6)–C(5)	122·3 (2)
C(1)–C(2)–C(3)	121·7 (1)	C(4)–N(7)–C(8)	119·8 (2)
C(2)–C(3)–C(4)	121·1 (1)	C(4)–N(7)–C(9)	122·0 (2)
C(3)–C(4)–C(5)	116·6 (2)	C(8)–N(7)–C(9)	116·5 (2)
C(3)–C(4)–N(7)	121·2 (2)	C(1)–C(10)–C(1′)	117·7 (1)

important factor for determining the conformation in (IV) would be the hydrogen bonding.

Comparison of the conformations of the dimethylamino groups in (I) and (II) reveals that η is not influenced by the introduction of a methylene group between two phenyl rings which disturbs the conjugation between them. This finding suggests that, in (I) and (II), the effect of the substituent plays a less important role in determining the conformation of the dimethylamino group. The conformation of the dimethylamino group in gaseous *N,N*-dimethylaniline with no substituent effect and no packing interaction is pyramidal, $\eta = 27°$ (Cervellati, Dal Borgo & Lister, 1982). Therefore, small η values in (I) and (II) would result from packing effects and cause a decrease of $d_{\rm CN}$.

In (I), the dihedral angle between the two phenyl rings is 13·0 (1)°. In *para*-substituted biphenyls with $R < 0{\cdot}06$ in the Cambridge Data File, the angles are widely distributed from 1·6° in 4-hydroxybiphenyl (Brock & Haller, 1984) to 39·4° in 4,4′-dichlorobiphenyl (Brock, Kuo & Levy, 1978). In spite of the wide deviation of the dihedral angles, the C—C inter-ring bond lengths are within the narrow range of

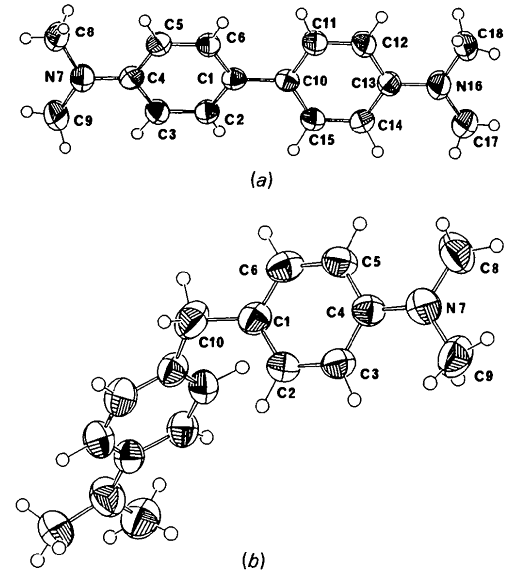

Fig. 1. *ORTEP* drawings (Davenport & Hall, 1987). C and N atoms are represented by thermal ellipsoids with 50% probability. (*a*) *N,N,N′,N′*-Tetramethylbenzidine (I), (*b*) 4,4′-methylenebis-(*N,N*-dimethylaniline) (II).

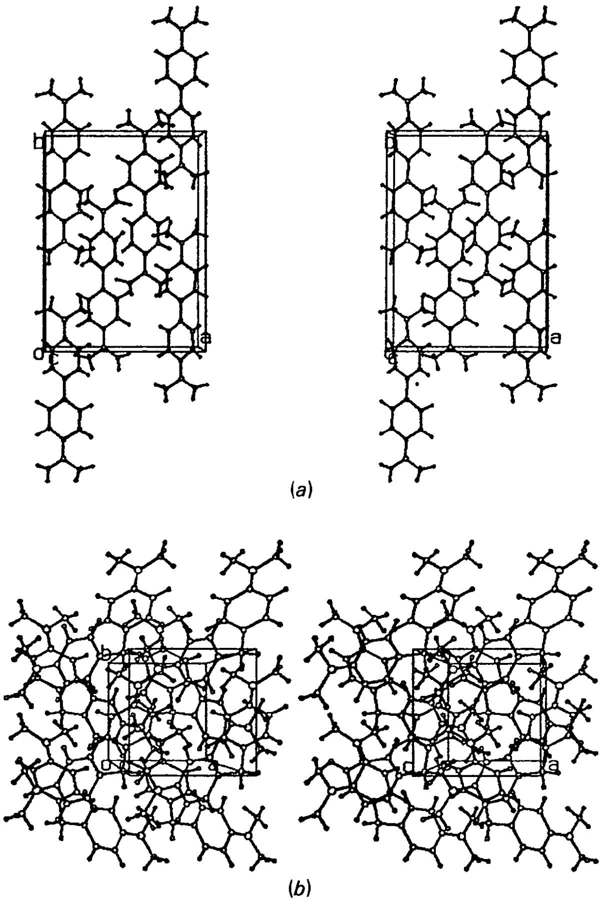

Fig. 2. Stereoview of the unit-cell packing for (*a*) (I) and (*b*) (II).

1·478–1·489 Å, probably because the attractive forces from π–π conjugation between the two phenyl rings are in competition with the repulsive forces between the pairs of the *ortho* H atoms.

The C(1)—C(10)—C(1′) bridge angle in (II) is larger than a regular tetrahedral angle, as with 115·3 (3)° in 4,4′-methylenebis(aniline) (Bel'skii, Rotaru & Kruchinin, 1983) and 116·7 (1)° in its sodium chloride complex (Swardstrom, Duvall & Miller, 1972). These large angles would result from the steric repulsion between the two phenyl rings.

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trans,trans-1,4-Bis[2-(3,4,5-trimethoxyphenyl)vinyl]benzene

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Abstract. $C_{28}H_{30}O_6$, $M_r = 462{\cdot}6$, monoclinic, $P2_1/a$, $a = 13{\cdot}227\ (3)$, $b = 5{\cdot}167\ (2)$, $c = 19{\cdot}217\ (7)$ Å, $\beta = 111{\cdot}07\ (3)°$, $V = 1225\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}264$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 8{\cdot}24$ mm^{-1}, $F(000) = 492$, room temperature, $wR = 0{\cdot}061$, $R = 0{\cdot}054$ for 1441 observed $[I \geq 3\sigma(I)]$ reflections out of 2408 measured, and 214 variables. The overall shape of the molecule is only semi-planar; the largest deviation from planarity is observed in the region of the double bonds. Packing is such that H atoms at the outer sides of one molecule point into π-orbital areas of neighbouring molecules. C(phenyl)—O lengths of in-plane methoxy groups are smaller, C(methyl)—O larger and C(phenyl)—O—C(methyl) angles larger than corresponding values of the out-of-plane methoxy group. Valence angles of the outer phenyl rings can be quantitatively reproduced using Domenicano & Murray-Rust [*Tetrahedron Lett.* (1979), pp. 2283–2286] parameters. The geometry of the central ring is influenced by a large-amplitude motion.

Introduction. Poly(arylenealkenylenes) constitute a group of compounds that are of interest because of their conducting properties, which depend *inter alia* upon the mobility of non-σ electrons in the solid. The latter is strongly influenced by the degree of planarity of the polymeric backbone and the availability of suitable contacts between individual molecules. The X-ray analysis of the title compound (Fig. 1), which is a model compound for substituted poly(1,4-phenylene–ethenylene), was undertaken to collect structural information useful in investigations of organic semiconductors. The compound was synthesized by a Wittig reaction.

Experimental. At room temperature a solution of 3·88 g (0·057 mol) sodium in 100 ml dry ethanol was added dropwise to a solution of 9·8 g (0·050 mol) 3,4,5-

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