Table 3. *Molecular geometry for* (3), *e.s.d.'s in parentheses*

(*a*) Unconstrained bond lengths (Å)

	Molecule *A*	Molecule *B*
S(4)–C(4)	1·815 (6)	1·813 (6)
S(5)–C(5)	1·826 (5)	1·819 (6)
C(4)–C(5)	1·523 (8)	1·549 (7)
C(4)–C(6)	1·527 (7)	1·509 (7)
C(5)–C(7)	1·526 (7)	1·520 (9)

(*b*) Unconstrained bond angles (°)

C(2)–S(4)–C(4)	103·9 (3)	101·9 (3)
C(3)–S(5)–C(5)	102·2 (2)	104·0 (3)
S(4)–C(4)–C(5)	114·5 (4)	111·3 (4)
S(4)–C(4)–C(6)	103·4 (4)	105·0 (6)
C(5)–C(4)–C(6)	112·4 (6)	112·3 (5)
S(5)–C(5)–C(4)	112·7 (4)	113·5 (4)
S(5)–C(5)–C(7)	103·8 (4)	105·3 (5)
C(4)–C(5)–C(7)	112·2 (5)	112·3 (5)

(*c*) Averaged values for endocyclic bond angles in the constrained section of molecules *A* and *B* (°)

C(1)–S(2)–C(2), C(1)–S(3)–C(3)	97·9
S(2)–C(2)–C(3), S(3)–C(3)–C(2)	116·0
S(4)–C(2)–C(3), S(5)–C(3)–C(2)	128·0

(*d*) Intra-annular torsion angles (τ) for the six-membered rings (°) (e.s.d.'s are less than 1°)

C(2*A*)–C(3*A*)	−3·1	C(3*B*)–C(2*B*)	2·4
C(3*A*)–S(5*A*)	21·0	C(2*B*)–S(4*B*)	20·7
S(5*A*)–C(5*A*)	−51·7	S(4*B*)–C(4*B*)	−54·9
C(5*A*)–C(4*A*)	66·0	C(4*B*)–C(5*B*)	68·2
C(4*A*)–S(4*A*)	−40·8	C(5*B*)–S(5*B*)	−39·1
S(4*A*)–C(2*A*)	8·9	S(5*B*)–C(3*B*)	3·4

C(4)–C(5) bonds are staggered (CH_3–C–C–CH_3, −59·8 and −55·1°; S–C–C–S, 66·0 and 68·2°); torsion angles in the six-membered rings are given in Table 3(*d*). There are only two short intermolecular S···S contacts, both between a pair of pseudo-centrosymmetrically related molecules in adjacent layers: S(5*A*)···S(3*B*, *x*, 1+*y*, *z*), 3·55 and S(3*A*)···S(5*B*, *x*, 1+*y*, *z*), 3·67 Å.

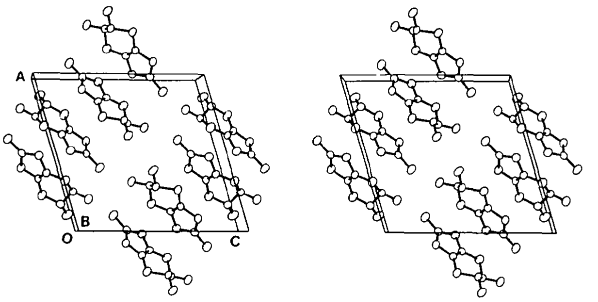

Fig. 2. Stereoview of the crystal packing of (3), H atoms omitted.

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Structure of 2-Methoxy-*N*-(4-nitrobenzylidene)-5-pyridylamine. II. Non-centrosymmetric Modification

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Abstract. $C_{13}H_{11}N_3O_3$, $M_r = 257{\cdot}2$, monoclinic, $P2_1$, $a = 3{\cdot}8566\,(5)$, $b = 19{\cdot}542\,(4)$, $c = 8{\cdot}066\,(1)$ Å, $\beta = 89{\cdot}37\,(1)°$, $V = 607{\cdot}9\,(6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}40$, $D_m = 1{\cdot}39$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 7{\cdot}62$ cm^{-1}, $F(000) = 268$, $R = 0{\cdot}0493$ for 1116 observed reflections. The molecule is not planar. The dihedral angle between the phenyl and the pyridyl rings is 35·7 (2)°. The conformation of the molecule differs from that of the centrosymmetric modification [Moustakali-Mavridis, Terzis & Hadjoudis (1987). *Acta Cryst.* C**43**, 1793–1795] but bond distances and angles are very similar, the highest deviations being observed in the bond lengths of the 'bridge' atoms connecting the two ring systems.

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Table 1. *Summary of data collection and structure refinement*

(*a*) Data collection (293 K)*	
Radiation	Cu $K\alpha$ (Ni-filtered)
Mode	θ–2θ scan
Scan range	1·8° plus α_1–α_2 divergence in 2θ
Scan rate (°min^{-1})	1·0–10·0
Background	$\frac{1}{4}$ of scan time at start and end of each scan
2θ range (°)	2·0–140·0
Range in *h,k,l*; min.	0,0,–9
max.	4,23,9
Total reflections measured	1369
Number of unique reflections	1194
Crystal dimensions (mm)	0·7 × 0·2 × 0·2
Absorption correction	None
(*b*) Structure refinement	
Reflections used ($F > 5\sigma_F$)	1116
Number of variables	204
Goodness of fit	0·71
R, *wR*	0·0493, 0·0676
R for all data	0·0512
Max. shift/e.s.d.	0·15 (for an H-atom position)
Max. density in difference map (e Å^{-3})	0·19
Min. density in difference map (e Å^{-3})	–0·29

* Unit-cell parameters were obtained by least-squares refinement of 15 reflections with $48 < 2\theta < 55°$. Syntex $P2_1$ autodiffractometer. Crystal stability and X-ray damage were monitored by measurement of three check reflections every 67 reflections. No damage to the crystal was observed.

Introduction. The title compound has been crystallized in two modifications, a centrosymmetric form (Moustakali-Mavridis, Terzis & Hadjoudis, 1987) and the present non-centrosymmetric one. The non-centrosymmetric crystals show a strong second harmonic generation effect. The determination of the structure of the non-centrosymmetric 2-methoxy-*N*-(4-nitrobenzylidene)-5-pyridylamine was carried out in order to attempt a quantitative treatment of the electro-optical effect.

Experimental. The title compound was prepared by condensation of 4-nitrobenzaldehyde and 2-methoxy-5-pyridylamine in ethanol. Single crystals in the form of elongated prisms were grown from a mixture of ethanol and chloroform. The density was measured by flotation in aqueous $ZnCl_2$. A summary of data collection and structure refinement is given in Table 1. Intensities were corrected for Lorentz and polarization effects.

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The structure was solved and refined with *SHELX*76 (Sheldrick, 1976). Refinement was by full-matrix weighted least squares [$\sum w(F_o - F_c)^2$ minimized, $w = 1/(\sigma_F^2 + 0{\cdot}01F^2)$]. Best *E* map ($E > 1{\cdot}2$) revealed 16 out of 19 non-H atoms. The additional three were found from a difference map; H atoms were similarly located at the end of isotropic refinement. Final refinement of the positional parameters of all atoms and anisotropic thermal parameters for non-H atoms with fixed isotropic thermal parameters for H atoms (1·25 times those of the atoms to which they were bonded) gave $R = 0{\cdot}0493$; $wR = 0{\cdot}0676$. The alternative enantiomeric structure converged to $R = 0{\cdot}0494$ and $wR = 0{\cdot}0677$ (Hamilton, 1964).

Discussion. Final coordinates and equivalent isotropic temperature factors are listed in Table 2.* Fig. 1 shows atom labelling and geometry for both the present non-centrosymmetric form and the centrosymmetric form

Table 2. *Coordinates for non-hydrogen atoms* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^4)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	*y*	*z*	U_{eq}
C(1)	3854 (5)	−4424 (0)	3166 (3)	438 (7)
C(2)	5306 (6)	−3773 (2)	3008 (3)	503 (7)
C(3)	6406 (6)	−3415 (2)	4390 (3)	506 (7)
C(4)	6003 (6)	−3720 (2)	5918 (3)	467 (7)
C(5)	4482 (6)	−4361 (2)	6125 (3)	497 (7)
C(6)	3387 (6)	−4709 (2)	4745 (3)	473 (7)
C(7)	2884 (6)	−4807 (2)	1666 (3)	497 (7)
C(8)	875 (6)	−5780 (2)	330 (3)	456 (7)
C(9)	−510 (6)	−5494 (2)	−1079 (3)	484 (7)
C(10)	−883 (5)	−6519 (2)	−2393 (3)	465 (7)
C(11)	434 (6)	−6867 (2)	−1024 (4)	571 (7)
C(12)	1309 (6)	−6495 (2)	347 (3)	537 (7)
C(13)	−3133 (6)	−6563 (2)	−5126 (3)	592 (8)
N(1)	1752 (5)	−5421 (2)	1777 (3)	489 (7)
N(2)	−1407 (5)	−5849 (2)	−2423 (3)	484 (7)
N(3)	7263 (6)	−3371 (2)	7393 (3)	599 (7)
O(1)	−1704 (5)	−6907 (2)	−3720 (3)	585 (6)
O(2)	6915 (7)	−3650 (2)	8733 (3)	946 (8)
O(3)	8795 (7)	−2831 (2)	7206 (3)	848 (7)

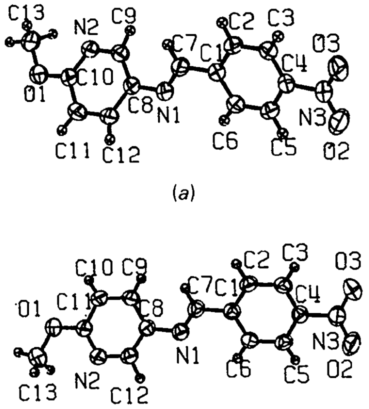

Fig. 1. *ORTEP* (Johnson, 1965) drawing of 2-methoxy-*N*-(4-nitrobenzylidene)-5-pyridylamine showing the atomic labelling and geometry for (*a*) non-centrosymmetric, (*b*) centrosymmetric modification.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44781 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Moustakali-Mavridis *et al.*, 1987). The orientation of the 2-methoxypyridyl ring with respect to the rest of the molecule is different in the two forms, exhibiting free rotation of the ring around N(1)—C(8), in accord with previous observations (Moustakali-Mavridis, Hadjoudis & Mavridis, 1980). In both forms the methoxy group is coplanar with the pyridyl ring with the methyl group *cis* to the ring N atom about C(10)—O(1). In this orientation unfavourable interactions between the H atoms of the methyl group and the pyridine ring are avoided.

In the present non-centrosymmetric modification the molecule deviates considerably from planarity. If we denote as *A* and *B* the planes of the phenyl and pyridyl rings respectively and *C* as the plane through atoms C(1), C(7), N(1) and C(8), then the angles between the normals to planes *A*, *B* and *C* are as shown in Table 3(*c*) for both centrosymmetric and non-centrosymmetric modifications. In the first, the sense of rotation of the aromatic rings *A* and *B* with respect to the central plane *C* is the same while it is reversed in the non-centrosymmetric case.

Table 3. *Molecular geometry*

(*a*) Bond lengths (Å)

C(1)—C(2)	1·395 (4)	C(11)—C(12)	1·369 (4)
C(1)—C(6)	1·400 (3)	C(13)—O(1)	1·433 (3)
C(1)—C(7)	1·474 (3)	N(3)—O(2)	1·216 (4)
C(2)—C(3)	1·386 (3)	N(3)—O(3)	1·218 (4)
C(3)—C(4)	1·376 (3)	C(2)—H(C2)	0·910 (10)
C(4)—C(5)	1·393 (4)	C(3)—H(C3)	0·814 (14)
C(4)—N(3)	1·460 (3)	C(5)—H(C5)	0·961 (9)
C(5)—C(6)	1·374 (3)	C(6)—H(C6)	0·988 (14)
C(7)—N(1)	1·279 (4)	C(7)—H(C7)	0·968 (9)
C(8)—N(1)	1·406 (3)	C(9)—H(C9)	0·988 (16)
C(8)—C(9)	1·380 (3)	C(11)—H(C11)	0·878 (16)
C(8)—C(12)	1·407 (4)	C(12)—H(C12)	0·987 (9)
C(9)—N(2)	1·336 (3)	C(13)—H1(Me)	1·089 (8)
C(10)—N(2)	1·325 (4)	C(13)—H2(Me)	0·876 (11)
C(10)—C(11)	1·398 (4)	C(13)—H3(Me)	0·931 (12)
C(10)—O(1)	1·352 (3)		

(*b*) Valence angles (°)

C(2)—C(1)—C(6)	119·5 (2)	N(1)—C(8)—C(12)	117·2 (2)
C(2)—C(1)—C(7)	119·6 (2)	C(9)—C(8)—C(12)	117·2 (2)
C(6)—C(1)—C(7)	120·9 (2)	C(8)—C(9)—N(2)	124·3 (2)
C(1)—C(2)—C(3)	120·9 (2)	C(9)—N(2)—C(10)	117·3 (2)
C(2)—C(3)—C(4)	118·0 (2)	N(2)—C(10)—C(11)	123·5 (2)
C(3)—C(4)—C(5)	122·7 (2)	N(2)—C(10)—O(1)	120·2 (2)
C(3)—C(4)—N(3)	119·5 (2)	C(11)—C(10)—O(1)	116·3 (2)
C(5)—C(4)—N(3)	117·8 (2)	C(10)—C(11)—C(12)	118·3 (2)
C(4)—C(5)—C(6)	118·7 (2)	C(8)—C(12)—C(11)	119·3 (2)
C(1)—C(6)—C(5)	120·2 (2)	C(10)—O(1)—C(13)	117·3 (2)
C(1)—C(7)—N(1)	120·6 (2)	C(4)—N(3)—O(2)	118·8 (3)
C(7)—N(1)—C(8)	119·7 (2)	C(4)—N(3)—O(3)	117·9 (2)
N(1)—C(8)—C(9)	125·5 (2)	O(2)—N(3)—O(3)	123·2 (3)

(*c*) Dihedral angles (°) involving planes *A B C* (see text)

	Centrosymmetric	Non-centrosymmetric
Between *A* and *B*	19·6	−35·7
Between *A* and *C*	3·2	4·8
Between *B* and *C*	22·7	−31·8

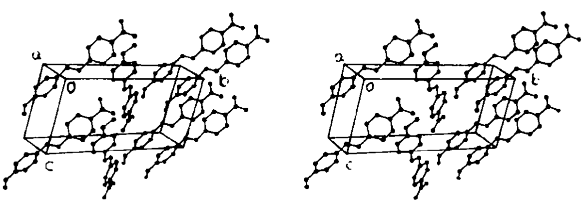

Fig. 2. Stereoscopic view of the molecular packing as viewed down the *a* axis (*ORTEP*; Johnson, 1965).

Table 3(*a*),(*b*) contains the bond lengths and angles with their e.s.d.'s. As in the case of *N*-(4-nitrobenzylidene)-4-dimethylaniline (Nakai, Shiro, Ezumi, Sakata & Kubota, 1976) the bridge distances C(1)—C(7) and N(1)—C(8) are shortened and N(1)—C(7) lengthened compared with the corresponding values in *N*-benzylideneaniline (1·496, 1·460 and 1·237 Å respectively) (Bürgi & Dunitz, 1970). This trend is attributed to the quinoid resonance forms that result in intramolecular charge transfer due to the electron affinity of the nitro groups. It is argued (Bürgi & Dunitz, 1971; Bernstein & Schmidt, 1972) that the bond lengths of the bridge depend on two opposing factors: (*a*) the amount of the quinoid resonance contributions, and (*b*) the rotation of the aniline ring about the N(1)—C(8) bond. The latter increases the overlap between the lone-pair electrons of the N atom and the π system of the ring and thus disrupts the quinoid resonance contribution. Comparison of the bond lengths and angles of the title compound in its two forms shows that the greatest deviations are in the bond lengths of the bridge. The shortening of the N(1)—C(8) bond and the lengthening of the N(1)—C(7) bond in the non-centrosymmetric modification compared with the centrosymmetric one might reflect a stronger interaction between the N atom lone pair and the pyridine π system because of the rotation of the latter.

A packing diagram is shown in Fig. 2. Intermolecular contacts are normal van der Waals interactions. The distance between adjacent molecules along the shortest axis, *a*, is 3·43 Å.

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