Configurational Isomerism in Crystalline Forms of Benzophenone Anils[1]

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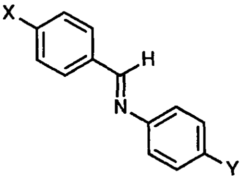
4-Methyl-*N*-(4-nitro-α-phenylbenzylidene)aniline, which in solution exists as a mixture of rapidly interconverting stereoisomers with *Z* and *E* configurations, is found in the solid state to have three crystalline forms. The **A** form consists of three independent molecules, all with the *Z* configuration, whereas the **B** (with two independent molecules) and **C** forms contain only molecules of the *E* configuration. The **B** and **C** forms at ambient temperature are converted into the **A** form, thus providing an example of rearrangement of the *E* to *Z* imine, which, because of the rapid approach to an equilibrium mixture in solution, can only be observed in the solid state as a controlled transition between isolable starting material and product.

Polymorphism (the existence of a substance in more than one crystalline form) is important in many areas of solid state chemistry.[2] Polymorphs whose molecules have significant structural differences are of particular interest and *conformational* polymorphism has been extensively studied by Bernstein and co-workers[2a] who have investigated carefully a family of compounds, the benzylidene anilines **1**, which have a particular tendency to crystallize as polymorphs. They found that individual molecules making up the two crystalline forms of such a compound had different angles of rotation of the aryl rings about the C–C and C–N single bonds, that is they were different conformers, but on dissolution the crystals gave identical conformer mixtures since rotation around the single bonds was very rapid once the rigidity provided by the solid state was removed. A structurally related group of compounds is exemplified by structures (*E*)- and (*Z*)-**2**, where Y can be any of a wide variety of substituents such as OH, OR, NHR, halogen, alkyl, or an aromatic ring. Such *configurational* isomers undergo interconversion at rates which vary with the substituents by more than 10^{14},[3,4,5] the rate being most sensitive to the nature of substituent Y.



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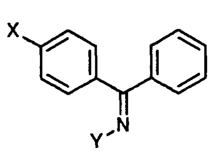
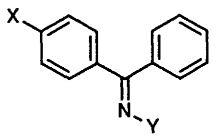
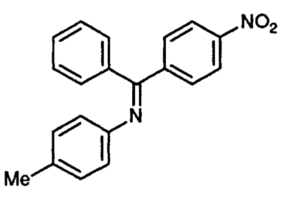


(*E*)-**2**

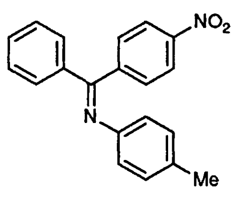


(*Z*)-**2**

We were particularly interested in certain members of this group, the diarylmethylene anilines, such as (*Z*)- and (*E*)-**3**. These compounds when dissolved, rapidly undergo interconversion; the equilibrium constants for these reactions are typically 1 or 2. However, these diarylmethylene anilines had been shown to give crystalline solids believed to consist of a single configuration.



(*E*)-**3**



(*Z*)-**3**

The parent compound **2** (with X = H, Y = Ph) has been found to exist in two polymorphic forms[6] one of whose crystal structures has been determined.[7] Also a crystal structure of the *N*-mesityl compound **2** (X = H, Y = 2,4,6-trimethylphenyl-) has been reported.[8] However, neither of these compounds has substituents which permit the existence of configurational isomers.

The present work was undertaken with the aim of studying substances crystallizing in more than one form and whose forms correspond to the two stereoisomers of **3**, *i.e.* configurational isomers. We were attracted to the *p*-nitro *p*′-methyl compound **3** because of an observation[9] that this compound existed in what appeared to be a mixture of two crystalline forms, one orange and one yellow, which, when dissolved, gave identical IR spectra. In this paper we report the isolation and determination of the crystal structures of crystalline forms of **3** which are configurational isomers.

Experimental

Synthesis of 4-*Methyl*-N-(4-*nitro*-α-*phenylbenzylidene*)*aniline* **3**.—The imine was prepared by condensation of *p*-nitrobenzophenone with *p*-toluidine in refluxing toluene in the presence of a catalytic amount of PCl_5. Recrystallization from absolute ethanol followed by sublimation at 140 °C (0.01 Torr; 1 Torr = 133.322 Pa) gave **3** as a yellow powder, m.p. 84–87 °C; $\delta_H(CDCl_3)$ 8.20–6.40 (13 H, m), 2.18 (3 H, s). CHN analyses agreed with the calculated values to within 0.3%. Recrystallization from ethanol or hexane–ether at 0 °C often gave a mixture of a yellow **A**, m.p. 91 °C and an orange crystalline form **3B**, m.p. 78–80 °C, while a second yellow form **3C**, m.p. 91 °C was in general obtained by crystallization from ethanol solution at room temperature.

X-Ray Structure Determination.—Samples of the three forms suitable for X-ray crystallography were obtained by recrystallization. Data were collected with a Syntex $P2_1$ automated four-circle diffractometer or on an Enraf-Nonius CAD-4 κ-axis instrument, and were corrected for Lorentz and polarization effects. Atomic scattering factors of Cromer *et al.*[10] were used for all non-hydrogen atoms and those of Stewart *et al.*[11] for the hydrogen atoms.

Table 1 Crystallographic data for compounds **3A**, **3B** and **3C**

	3A	3B	3C
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	6	4	4
Formula		$C_{20}H_{16}N_2O_2$	
M		316.4	
a/Å	14.739(9)	11.617(1)	11.683(4)
b/Å	15.033(4)	14.457(2)	10.433(3)
c/Å	12.487(4)	11.286(2)	14.166(3)
α/°	106.80(2)	104.89(1)	90
β/°	106.02(4)	105.14(1)	92.81(2)
γ/°	90.44(4)	104.34(1)	90
No. reflections for 1 sq. fit for cell constants	25	15	15
V/Å^3	2535(4)	1664(1)	1725(2)
d/g cm^{-3}	1.24	1.26	1.22
Cryst. form	Prism	Prism	Tabular
Size mm	1; 0.5; 0.3	0.16; 0.12; 0.21	0.5; 0.3; 0.3
	(Hexane–ether)		Ethanol
Data collection			
Diffractometer	CAD-4	$P2_1$	$P2_1$
Radiation	Mo-Kα[a]	Cu-Kα[b]	Mo-Kα[a]
μ/cm^{-1}	0.46	5.83	0.46
Scan mode	$\omega/2\theta$	ω/θ	ω/θ
Range 2θ°	2–51	3–130	3–50
Scan rate/° m^{-1}	2.4–16	2–19.5	2–19.5
Standard reflections monitored		three of every one hundred	
Unique measurements	9396	5661	3057
'Observed' reflections	4901	2880	981
Structure solution	RANTAN	RANTAN	MULTAN 80
Refinement	Block-diagonal	Block-diagonal	Full-matrix
Hydrogen atoms		(Calculated positions; single B_{iso} varied)	
Weights	$1/[\Sigma ArTr(x)]$[c]	$a/[\sigma^2(F_0) + (bF_0)^2]$[d]	
$(\rho_o-\rho_c)$ range	±0.22	±0.17	±0.19
R	0.049	0.045	0.059
R_w	0.053	0.062	0.070
GOF		2.01	1.73

[a] λ = 0.717 07 Å, graphite monochromated. [b] λ = 1.541 78 Å. [c] Tr(x) is the Chebychev polynomial; $x = |F_o|/|F_o|_{max}$, Ar values 23.6, 19.6, −12.0, −10.9. [d] For **3B**, a = 1.86, b = 0.0245; for **3C**, a = 8.70, b = 0.028.

All three crystal structures were solved by direct methods, using variously the RANTAN,[12] DIRDIF,[13] CRYSTALS[14,15] and MULTAN 80[16] programs.[1] The determination and refinement of the structure of **3A** caused some difficulties which were resolved by the use of CRYSTALS. A summary of the data collection, refinement procedures and results is given in Table 1. Final values of the atomic coordinates are given in Tables 2–4.*

FTIR Spectra of the Crystalline Forms of **3**.—These were obtained in Nujol mulls with a Nicolet 7000 FTIR spectrophotometer. Absorptions of particular interest because they permitted distinction among the three forms are as follows: **3A**, 1630, 1615, 736, 701 and 694; **3B**, 1620, 911, 730, 702 and 696; **3C**, 1620, 912, 731 and 701 cm^{-1}.

Interconversion of the Crystalline Forms of **3**.—A sample of **3C** which had been kept under ambient conditions for two years was shown to be 50% converted into **3A** on the basis of the IR spectrum in Nujol. In another experiment a similar change had occurred with a recently synthesized sample of **3C** that had been kept in Nujol for six days. When a Nujol mull of **3C** was heated at 68–74 °C for 4 h and then left at room temperature for 75 min, it was shown by FTIR spectroscopy to be approximately 60% converted into **3A**. When the heating was continued for an additional 2½ h there was complete conversion into **3A**.

A ground sample of **3B**, when heated at 58–61 °C for 4 h gave an X-ray powder diffraction photograph (Ni-filtered Cu-Kα radiation) identical with that of **3C** obtained by crystallization. This experiment was repeated four times but on one occasion the product was found to be **3A**, suggesting that **3C** is a metastable product at this temperature. A sample of **3B** in Nujol was completely transformed into **3A** after four days as shown by FTIR spectroscopy.

An attempt to test directly the use of IR absorption in the 700 cm^{-1} region by comparing the spectra of the Z form, **3A** with those of the *anti* forms **3B** and **3C** was unsuccessful because of the lack of sufficient differentiation of spectra prepared either in Nujol mull or KBr pellets.†

Results and Discussion

On repetition of the earlier work[9] we found not two, but three crystalline forms of **3** which we have designated **3A**, **3B** and **3C**. One, **3A**, crystallized in space group $P\bar{1}$ with six molecules per unit cell (three independent molecules). All three molecules in this form had the Z configuration. The crystal structure is shown in Fig. 1. The second form, **3B**, crystallized in the same space group. The four molecules per cell (two independent

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* Thermal parameters, bond lengths and angles and hydrogen atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre. For details see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1991. Structure factor tables are available from the authors on request.

† A possible complication is partial interconversion of the polymorphs during sample preparation.

Table 2 Final atomic coordinates for the three independent molecules in **3A**[a]

	x/*a*	*y*/*b*	*z*/*c*
N(1)	0.334 0(2)	0.328 0(2)	0.480 6(2)
C	0.423 9(2)	0.340 2(2)	0.525 9(3)
C(1A)	0.472 3(2)	0.400 6(2)	0.648 1(3)
C(2A)	0.527 1(3)	0.362 2(2)	0.729 6(3)
C(3A)	0.571 9(3)	0.418 3(3)	0.842 0(3)
C(4A)	0.561 2(3)	0.511 1(3)	0.869 9(3)
C(5A)	0.509 6(3)	0.551 6(3)	0.790 8(4)
C(6A)	0.464 4(2)	0.495 3(3)	0.679 7(4)
N(2)	0.608 7(4)	0.571 6(3)	0.990 0(4)
O(1)	0.588 6(3)	0.649 1(3)	1.020 7(3)
O(2)	0.667 9(2)	0.539 7(4)	1.048 4(4)
C(1B)	0.271 0(2)	0.366 0(3)	0.547 2(3)
C(2B)	0.213 8(3)	0.432 3(3)	0.517 2(4)
C(3B)	0.146 4(3)	0.463 0(4)	0.574 4(5)
C(4B)	0.133 8(3)	0.428 0(4)	0.659 5(5)
C(5B)	0.190 9(4)	0.362 0(5)	0.688 0(4)
C(6B)	0.260 2(3)	0.331 2(4)	0.634 3(4)
C(7B)	0.056 8(4)	0.457 9(5)	0.719 1(6)
C(1C)	0.483 4(2)	0.295 9(2)	0.450 6(3)
C(2C)	0.579 0(2)	0.327 3(3)	0.480 0(3)
C(3C)	0.632 3(3)	0.289 2(3)	0.405 3(4)
C(4C)	0.592 4(3)	0.220 3(3)	0.302 7(3)
C(5C)	0.498 3(3)	0.187 5(3)	0.273 5(3)
C(6C)	0.444 3(2)	0.224 4(3)	0.346 7(3)
N(1′)	0.133 6(2)	0.113 5(2)	0.107 1(2)
C′	0.184 5(2)	0.167 1(2)	0.080 0(3)
C(1A′)	0.179 3(2)	0.270 2(2)	0.106 7(3)
C(2A′)	0.098 0(2)	0.306 6(2)	0.056 3(3)
C(3A′)	0.093 2(2)	0.401 4(2)	0.083 5(3)
C(4A′)	0.169 0(2)	0.459 5(2)	0.162 9(3)
C(5A′)	0.250 4(2)	0.425 9(2)	0.214 7(3)
C(6A′)	0.255 4(2)	0.331 3(2)	0.184 7(3)
N(2′)	0.163 7(2)	0.560 7(2)	0.194 8(3)
O(1′)	0.097 8(2)	0.591 0(2)	0.137 7(3)
O(2′)	0.224 0(2)	0.610 5(2)	0.277 9(3)
C(1B′)	0.068 9(2)	0.150 6(2)	0.171 5(3)
C(2B′)	−0.027 3(2)	0.123 9(2)	0.120 3(3)
C(3B′)	−0.090 2(2)	0.156 4(3)	0.183 1(3)
C(4B′)	−0.060 2(3)	0.213 2(3)	0.297 1(3)
C(5B′)	0.035 8(3)	0.237 7(3)	0.348 0(3)
C(6B′)	0.100 2(2)	0.206 6(3)	0.286 2(3)
C(7B′)	−0.130 4(3)	0.246 9(4)	0.364 3(4)
C(1C′)	0.253 2(2)	0.125 0(2)	0.017 0(3)
C(2C′)	0.286 8(2)	0.169 8(2)	−0.048 5(3)
C(3C′)	0.349 3(3)	0.129 1(3)	−0.109 5(3)
C(4C′)	0.378 6(3)	0.044 1(3)	−0.104 0(4)
C(5C′)	0.346 4(3)	−0.000 6(3)	−0.039 0(4)
C(6C′)	0.283 4(3)	0.038 7(2)	0.021 2(3)
N(1″)	0.103 2(2)	−0.184 6(2)	0.146 4(2)
C″	0.193 2(2)	−0.171 3(2)	0.174 8(3)
C(1A″)	0.253 2(2)	−0.109 1(2)	0.290 4(3)
C(2A″)	0.312 0(2)	−0.147 1(2)	0.370 0(3)
C(3A″)	0.368 9(2)	−0.089 8(2)	0.475 6(3)
C(4A″)	0.366 9(2)	0.004 4(2)	0.498 8(3)
C(5A″)	0.308 8(2)	0.045 0(2)	0.422 3(3)
C(6A″)	0.251 8(2)	−0.013 6(2)	0.317 7(3)
N(2″)	0.429 0(2)	0.065 7(2)	0.610 9(3)
O(1″)	0.481 2(2)	0.029 4(2)	0.676 7(2)
O(2″)	0.424 8(2)	0.149 2(2)	0.632 4(3)
C(1B″)	0.050 7(2)	−0.148 6(2)	0.226 9(3)
C(2B″)	0.050 6(3)	−0.187 2(3)	0.314 1(3)
C(3B″)	−0.011 0(3)	−0.160 1(3)	0.380 8(4)
C(4B″)	−0.072 5(3)	−0.093 4(3)	0.363 5(3)
C(5B″)	−0.070 1(3)	−0.054 6(3)	0.277 7(4)
C(6B″)	−0.010 3(3)	−0.081 8(3)	0.208 9(3)
C(7B″)	−0.140 7(3)	−0.066 5(3)	0.435 8(4)
C(1C″)	0.242 5(2)	−0.218 9(2)	0.088 1(3)
C(2C″)	0.194 6(2)	−0.292 1(3)	−0.008 5(3)
C(3C″)	0.239 3(3)	−0.335 9(3)	−0.090 6(3)
C(4C″)	0.330 5(3)	−0.307 0(3)	−0.078 3(3)
C(5C″)	0.378 8(3)	−0.235 0(3)	0.016 2(4)
C(6C″)	0.335 3(2)	−0.190 2(2)	0.100 3(3)

[a] Primes and double primes are used to distinguish atoms in the three independent molecules [*e.g.* N(1), N(1′) and N(1″)].

Table 3 Final atomic coordinates for the two independent molecules in **3B**[a]

	x/*a*	*y*/*b*	*z*/*c*
O(1)	0.409 1(3)	−0.413 5(2)	−1.258 1(3)
O(2)	0.461 2(3)	−0.298 7(2)	−1.068 5(3)
N(1)	0.807 3(2)	−0.640 4(2)	−0.976 8(2)
N(2)	0.472 5(3)	−0.372 8(3)	−1.140 9(3)
C	0.826 3(3)	−0.547 6(2)	−0.915 0(3)
C(1A)	0.737 5(3)	−0.499 6(2)	−0.975 1(3)
C(2A)	0.644 0(3)	−0.554 9(3)	−1.097 9(3)
C(3A)	0.559 1(3)	−0.512 3(3)	−1.153 8(3)
C(4A)	0.566 2(3)	−0.416 3(3)	−1.084 7(3)
C(5A)	0.657 3(3)	−0.359 6(3)	−0.963 8(3)
C(6A)	0.743 5(3)	−0.401 9(3)	−0.910 6(3)
C(1B)	0.879 6(3)	−0.695 3(2)	−0.922 9(3)
C(2B)	0.864 9(3)	−0.723 2(2)	−0.817 8(3)
C(3B)	0.925 6(3)	−0.787 3(3)	−0.777 1(3)
C(4B)	1.000 4(3)	−0.824 9(3)	−0.839 8(3)
C(5B)	1.014 6(3)	−0.795 5(3)	−0.943 9(3)
C(6B)	0.953 8(3)	−0.733 0(3)	−0.987 3(3)
C(7B)	1.063 6(4)	−0.896 1(3)	−0.797 9(4)
C(1C)	0.933 7(3)	−0.483 2(3)	−0.789 3(3)
C(2C)	0.917 4(3)	−0.460 5(3)	−0.670 3(3)
C(3C)	1.020 3(3)	−0.399 9(3)	−0.557 0(3)
C(4C)	1.138 3(3)	−0.363 0(3)	−0.563 5(3)
C(5C)	1.153 2(3)	−0.385 7(3)	−0.681 4(3)
C(6C)	1.052 6(3)	−0.446 4(3)	−0.794 6(3)
O(1′)	0.690 6(3)	−0.189 2(3)	−0.092 7(3)
O(2′)	0.744 9(3)	−0.061 1(3)	0.082 7(3)
N(1′)	0.464 4(2)	0.169 0(2)	−0.319 6(3)
N(2′)	0.686 8(3)	−0.106 0(3)	−0.032 4(4)
C′	0.408 4(3)	0.075 5(3)	−0.339 8(3)
C(1A′)	0.473 4(3)	0.027 5(2)	−0.253 7(3)
C(2A′)	0.441 7(3)	−0.076 9(3)	−0.290 3(3)
C(3A′)	0.510 8(3)	−0.122 0(3)	−0.219 0(4)
C(4A′)	0.609 4(3)	−0.059 6(3)	−0.106 1(3)
C(5A′)	0.639 9(3)	0.043 2(3)	−0.063 7(3)
C(6A′)	0.573 5(3)	0.088 2(3)	−0.138 2(3)
C(1B′)	0.410 9(3)	0.221 8(2)	−0.396 0(3)
C(2B′)	0.297 1(3)	0.237 2(3)	−0.399 2(3)
C(3B′)	0.254 5(3)	0.296 1(3)	−0.466 8(3)
C(4B′)	0.322 1(3)	0.342 4(3)	−0.532 7(3)
C(5B′)	0.435 9(4)	0.326 5(3)	−0.527 9(4)
C(6B′)	0.480 8(3)	0.268 4(3)	−0.459 5(3)
C(7B′)	0.275 9(4)	0.406 6(3)	−0.606 7(4)
C(1C′)	0.286 9(3)	0.008 0(2)	−0.449 7(3)
C(2C′)	0.179 1(3)	−0.032 2(3)	−0.424 0(3)
C(3C′)	0.069 3(3)	−0.095 9(3)	−0.526 8(4)
C(4C′)	0.066 5(4)	−0.119 9(3)	−0.652 5(4)
C(5C′)	0.172 7(4)	−0.079 9(3)	−0.678 5(4)
C(6C′)	0.283 3(3)	−0.015 4(3)	−0.576 5(3)

[a] Primes denote atoms in a second independent molecule.

molecules) making up this structure had the *E* configuration. Thus the two crystalline forms constitute configurational isomers. The structure of **3B** is shown in Fig. 2. The third form, **3C**, crystallizing in space group $P2_1/c$ with $Z = 4$ (one independent molecule) was again made up of *E* molecules. The arrangement in the crystal is shown in Fig. 3. It is striking that, although the free energies of (*Z*)- and (*E*)-**3** in solution are nearly equal, the molecular configuration found in the solid state is highly dependent on the crystal structure. Note that only the crystal structure of **3A** contained molecules of the *Z* configuration; structures **3B** and **3C**, as well as a number of other related imines whose crystal structures have been determined[1] contain only molecules of the *E* configuration.

It was found that both **3B** and **3C**, when allowed to stand for some days (or faster when suspended in Nujol) were converted into **3A**, establishing that **3A** is the most stable form at ambient temperature. These conversions are of particular interest because they demonstrate the use of the solid state to effect conversions of essentially pure (*E*)-**3** into pure (*Z*)-**3** even though each isomer in solution gives in a short time an equilibrium mixture of the two. This use of the immobilization provided by the solid state to permit isolation of configurational isomers of **3** which are in rapid equilibrium in solution has many isolated examples in the literature[17] but has received little systematic study.

Molecular Structures in **3A**, **3B** *and* **3C**.—A stereo picture of one of the molecules of **3A** is shown in Fig. 4, which indicates the general system of atom numbering for all three polymorphs. Bond lengths and angles are in reasonable agreement with those of the earlier structures.[7,8] The early difficulty in demonstrating the existence of *Z* and *E* isomers of unsymmetrically substituted anils such as **3A** and **3B** had led to occasional speculation that aryl–aryl steric repulsion together with ease of bending of the *N*-aryl group might make the C=N–C bond angle nearly 180°. However, this angle in the six crystallographically independent molecules of **3A**, **3B** and **3C**, as well as in the previously studied unsubstituted amine and *N*-mesityl compound, lies between 119 and 122°, values not significantly different from the corresponding angles found in structures of the unhindered benzylideneaniline (120°), and its carboxy (116°) and methyl nitro (121°) derivatives studied by Bürgi and Dunitz.[18]

Table 4 Final atomic coordinates in form **3C**

	x/*a*	*y*/*b*	*z*/*c*
O(1)	−0.283 3(6)	0.522 5(8)	0.552 6(6)
O(2)	−0.195 7(8)	0.505 4(9)	0.683 9(6)
N(1)	0.128 5(4)	0.162 2(5)	0.346 7(4)
N(2)	−0.208 4(7)	0.479 9(8)	0.601 6(7)
C	0.131 9(5)	0.173 1(6)	0.437 0(5)
C(1A)	0.044 0(5)	0.251 2(6)	0.480 8(5)
C(2A)	0.043 5(6)	0.272 1(6)	0.578 4(5)
C(3A)	−0.036 5(7)	0.347 4(7)	0.618 0(5)
C(4A)	−0.120 1(6)	0.400 2(7)	0.559 2(7)
C(5A)	−0.125 7(6)	0.381 8(7)	0.463 3(6)
C(6A)	−0.041 9(6)	0.307 5(6)	0.424 2(5)
C(1B)	0.211 3(6)	0.088 8(7)	0.301 3(5)
C(2B)	0.217 2(6)	−0.042 4(8)	0.311 6(5)
C(3B)	0.297 5(7)	−0.112 4(7)	0.262 4(5)
C(4B)	0.371 5(6)	−0.055 3(8)	0.203 7(5)
C(5B)	0.364 5(6)	0.076 9(8)	0.193 1(5)
C(6B)	0.285 6(6)	0.147 6(7)	0.240 5(5)
C(7B)	0.456 3(6)	−0.131 2(7)	0.151 5(5)
C(1C)	0.225 5(5)	0.114 9(6)	0.500 0(4)
C(2C)	0.201 1(6)	0.010 6(7)	0.555 3(5)
C(3C)	0.287(1)	−0.045 5(9)	0.611 4(6)
C(4C)	0.392 8(10)	0.005(1)	0.615 7(6)
C(5C)	0.418 8(7)	0.109 7(9)	0.562 8(7)
C(6C)	0.333 6(6)	0.165 0(7)	0.503 6(5)

It had been noted earlier[7,8] that the relatively unhindered *anti* *C*-phenyl group in the benzylideneanilines studied tended to be nearly coplanar with the plane of the bonds through the central C atom. The dihedral angles of the structures reported here, together with those of the earlier structures are summarized in Table 5 which shows that this tendency is even more pronounced in the crystalline isomers of **3**. In fact, the eight molecules found in these five structures have rather similar conformations. The rings *syn* to one another seriously interfere with each other and are mostly turned 60° or more out of the central plane.

Crystal Packing.—The volumes per molecule of the three forms are in the order **B** (416) < **A** (422) < **C** (432). There seem to be no chemically interesting close contacts in the structures of **3A**, **3B** and **3C**.

The discovery of three crystallographically independent molecules of **3A** in the space group $P\bar{1}$ is unusual, but by no means without precedent. A search of the Cambridge Crystallographic Data Base[19] revealed that of the 13 394 compounds reported in the space group $P\bar{1}$, there were 105 examples with six or more molecules per unit cell. Even after eliminating metal-containing compounds and compounds with –OH, –NH or $-NH_2$ groups that might be able to form some extended hydrogen-bonded system, 23 structures remained. Of the latter, only one molecule, *N*-(biphenyl-2,2′-diylvinylidene)-4-bromoaniline[20] bears any structural resemblance to compound **3A**.

The structures described above introduce a semantic problem which we have tried to avoid. McCrone[21] has defined a polymorph as 'a solid crystalline phase of a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state' and has gone on to exclude specifically geometrical

Table 5 Extent of rotation (°) of rings out of molecular plane

	C-Aryl rings		
Structure	*E*	*Z*	*N*-Aryl rings
3A	16.4	65.7	70.2
	20.9	66.9	66.7
	14.7	72.2	74.4
3B	5.8	79.2	68.4
	16.7	67.6	62.0
3C	1.7	73.9	67.0
2[a]	29.3	48.3	67.8
2[b]	15.3	61.9	75.5

[a] **2** X = H, Y = Ph; ref. 7. [b] **2** X = H, Y = 2,4,6-trimethylphenyl; ref. 8.

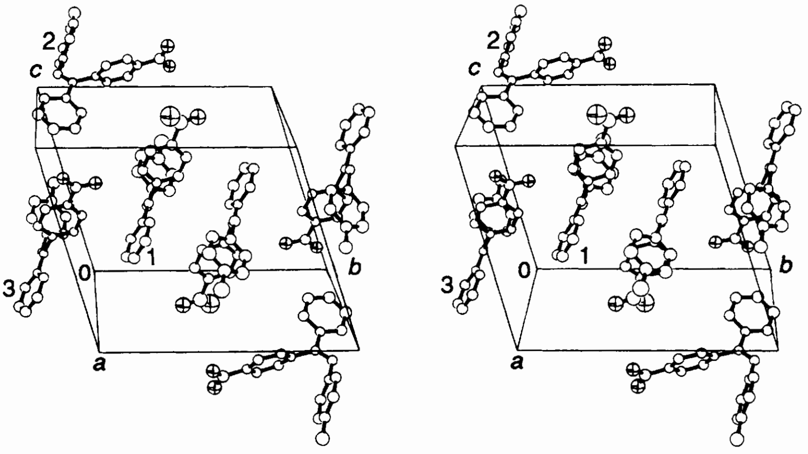

Fig. 1 Stereoscopic view of the packing of the molecules in form **3A**. The three independent reference molecules are designated by the numbers (1), (2) and (3).

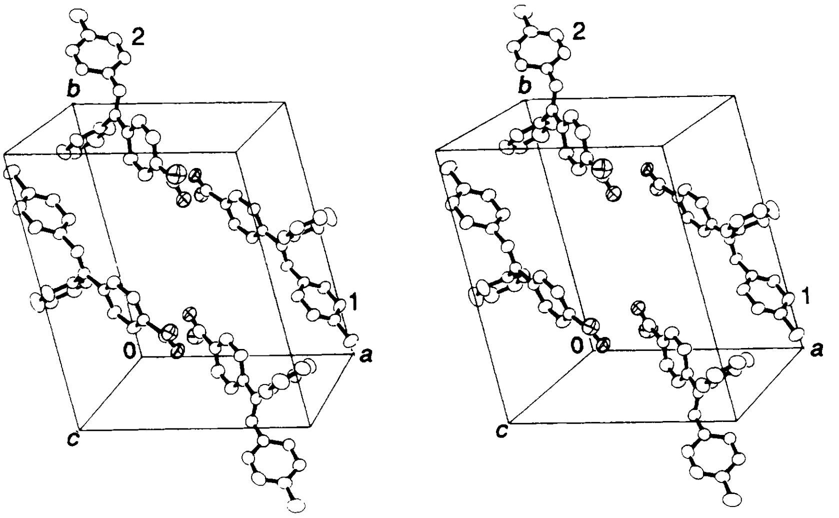

Fig. 2 Stereoscopic view of the structure of form **3B**. The two independent reference molecules are labelled by (1) and (2).

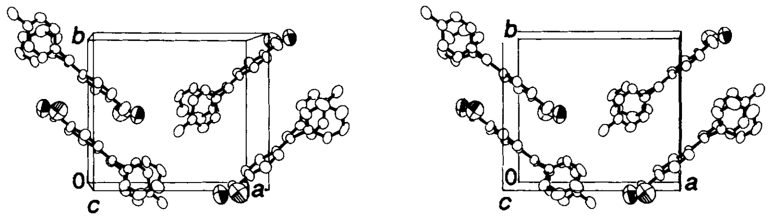

Fig. 3 Stereoscopic view of the packing in the crystal of form **3C**

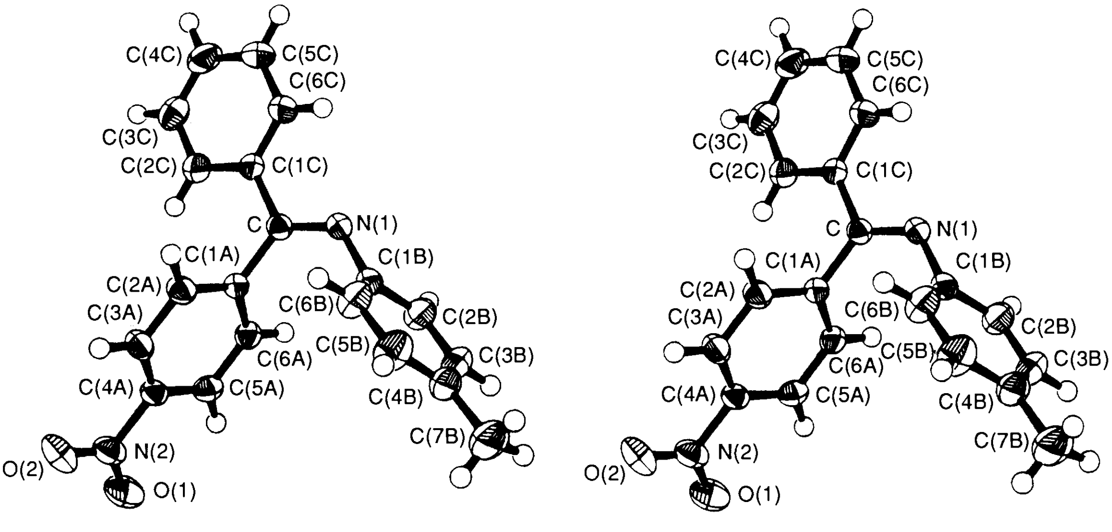

Fig. 4 Stereoscopic view of one of the independent molecules (*Z* configuration) in form **3A**

isomers 'even though interconvertible and reversibly so'. We have therefore avoided calling **3A**, **3B** and **3C**, 'polymorphs' even though **3B** and **3C** are clearly conformational polymorphs of each other by McCrone's definition and the differentiation from the conformational polymorphism studied by Bernstein[2] seems to be based on a technicality derived from the organic chemist's use of 'conformation' and 'configuration'.

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