

The quinuclidine ring takes a skewed conformation as found in (2) and (3); when viewed down the N(16)–C(19) direction the bonds C(19)–C(18), C(19)–C(20) and C(19)–C(22) are rotated by 7.4 (2), 8.9 (2) and 6.9 (2)° from the eclipsed position of bonds N(16)–C(17), N(16)–C(15) and N(16)–C(22), respectively. The bond lengths and angles in the ring are normal for an sp^3 – sp^3 single bond: on average C–C = 1.535 (4), C–N = 1.480 (4) Å; C–C–C = 108.3 (2), C–N–C = 108.8 (2)°.

Conformations around the C(4)–C(13) and C(13)–C(15) bonds are mainly determined by the intramolecular requirements rather than the crystallographic environments:

τ_1 [C(3)–C(4)–C(13)–C(15)] = –99.3 (3) for (1), –100.3 (4) for (2) and –109 (2)° for (3); τ_2 [O(14)–C(13)–C(15)–N(16)] = 75.9 (3) for (1), 74.8 (4) for (2) and 48 (2)° for (3). The τ_2 results in the O(14)···N(16) distances of 3.093 (3) for (1), 3.110 (4) for (2) and 2.84 (2) Å for (3). A similar conformation of O with respect to N is found in procaine and related compounds (Kashino, Ikeda & Haisa, 1982).

On the other hand, the conformation in the side chains is varied by the crystal packing:

τ_3 [C(5)–C(6)–O(11)–C(12)] = 179.0 (3) for (1), –5.8 (6) for (2) and 8(3)° for (3); τ_4 [C(21)–C(22)–C(23)–C(24)] = 109.6 (4) for (1), 123 (1) for (2) and 180 (4)° for (3).

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α -(*p*-Bromobenzoyloxy)- β -phenylazostilbene, $C_{27}H_{19}BrN_2O_2$ *

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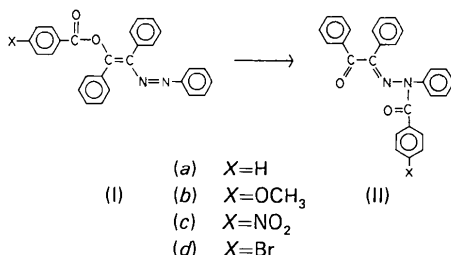
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Abstract. $M_r = 483.36$, monoclinic, $P2_1/c$, $Z = 4$, $a = 10.210$ (2), $b = 16.594$ (3), $c = 14.546$ (3) Å, $\beta = 104.64$ (2)°, $V = 2384.4$ Å³, $D_x = 1.346$ Mg m⁻³, Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å, $\mu = 2.80$ mm⁻¹), $T = 298$ K, $F(000) = 984$. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares methods using 3589 observed independent diffractometer-measured intensity data to $R = 0.072$, $R_w = 0.044$. Crystals were prepared by the reaction of

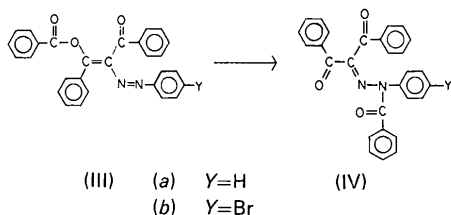
benzil monophenylhydrazone with *p*-bromobenzoyl chloride. The configuration at the C=C bond is *trans*. This supports the proposed mechanism for the thermal rearrangement to the aroylhydrazone in which isomerization to the *cis* form is the rate-determining step and migration of the aroyl group a fast second step.

Introduction. α -Benzoyloxy- β -phenylazostilbene (*Ia*) rearranges in quantitative yield to benzil monobenzoylphenylhydrazone (*IIa*) in solution and in the solid state (Russell & Weisleder, 1967).

* α -Phenyl- β -phenylazostyryl *p*-bromobenzoate.



Kinetic studies in decalin solution showed that the reaction was first order and remarkably insensitive to substituents in the migrating group. It was proposed that the starting material is a *trans* stilbene and that the rate-determining step of the rearrangement is isomerization to the *cis* form, bringing the ϕ -C- and the -N=N- ϕ groups closer together, followed by a rapid intramolecular rearrangement to the benzoylhydrazone (Russell, Strothkamp & Kasprisin, 1969). The rearrangement might occur during the isomerization and before the *cis* isomer actually forms. This suggestion was corroborated by the work of Pendergrass, Curtin & Paul (1972) who studied the analogous rearrangement of (IIIa,b) to (IVa,b).



They showed crystallographically that (IIIb) has a *trans* configuration at both the C=C and the N=N double bonds. An X-ray study of (Id) was undertaken to establish the configuration of the starting material in the rearrangement of (I) to (II).

Experimental. The title compound was prepared by the reaction of benzil monophenylhydrazone with *p*-bromobenzoyl chloride; crystals suitable for X-ray work obtained by dissolving the compound in ethanol and allowing the solvent to evaporate slowly; intensity data measured on an Enraf-Nonius CAD-4 automated diffractometer, monochromated Cu K α radiation, crystal 0.32 \times 0.30 \times 0.40 mm, unit-cell parameters determined by a least squares fit of the angular settings for 15 reflections (263, 354, 425, 264, 354, 263, 171, 172, 181, 180, 181, 182, 432, 432 080), ω -2 θ scanning mode; $\theta \leq 73^\circ$ for the range $0 \leq h \leq +12$, $0 \leq k \leq +20$, $-17 \leq l \leq +17$; systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ uniquely defined the space group $P2_1/c$; relative ranges of intensity variation for standard reflections $12\bar{3}$ and 022 were 5.3 and 4.7% respectively; intensities corrected for Lorentz-polarization effects but not for absorption; of 4741 possible independent reflections, 3589 were accepted as

observed on the criterion $I > 1.5\sigma(I)$; structure solved by heavy-atom method and refined by Fourier and block-diagonal least-squares methods, a difference electron density map showed the positions of all the H atoms, refinement was then continued on all positional parameters, anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms; in the final cycle $R = 0.072$ and $R_w = 0.044$ for the observed reflections only, mean and maximum shift/e.s.d. values were 0.161 and 0.571, $S = 1.19$, the function minimized was $\sum w(|F_o| - k|F_c|)^2$, where $w = 1/\sigma^2(F)$ was obtained from counting statistics for the observed reflections, unobserved reflections weighted zero, maximum and minimum peak heights in the final difference Fourier synthesis were 0.28 and -0.73 e \AA^{-3} , the latter in the region of the Br atom; scattering factors for the non-H atoms from *International Tables for X-ray Crystallography* (1962), that for H from Stewart, Davidson & Simpson (1965); all structural calculations performed with the NRC System (Ahmed, Hall, Pippy & Huber, 1973).

Discussion. The atomic coordinates, equivalent isotropic B 's for the non-H atoms (Willis & Pryor, 1975) and the B 's for the H atoms are given in Table 1.*

The structure presented here shows that α -(*p*-bromobenzoyloxy)- β -phenylazostilbene has indeed the *trans* configuration at the C=C and at the N=N bonds, as shown in Fig. 1. Bond distances and bond angles involving atoms N(1), N(2), C(1), C(2) and O(1) do not vary significantly from standard values (see Table 2). A least-squares mean plane of atoms C(1), C(2), N(1) and N(2) has a maximum deviation of 0.055 (3) Å for N(1), while that for atoms N(1), C(1), C(2), C(3), C(9) and O(1) has a maximum deviation of 0.077 (2) Å for O(1). Torsion angles involving the C=C bond are -4.8 (3) $^\circ$ for C(9)-C(2)-C(1)-N(1), 177.4 (3) $^\circ$ for C(9)-C(2)-C(1)-C(3), 171.4 (3) $^\circ$ for O(1)-C(2)-C(1)-N(1), and -6.4 (3) $^\circ$ for O(1)-C(2)-C(1)-C(3). All C-H distances fall within the range of standard values. There are no significantly short intermolecular contacts which might favor intermolecular rearrangement. The minimum nonbonded intramolecular distance is 2.245 (3) Å between O(1) and O(2). The distance between the rearrangement termini in the crystal, N(2)-C(21) = 5.414 (5) Å, explains the low rate of thermal rearrangement in the solid compared with the melt or in solution (Russell *et al.*, 1967, 1969). The packing is shown in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38171 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$, for H $\times 10^3$), equivalent isotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for H atoms

The form of the isotropic thermal factors used was $\exp(-B\sin^2\theta/\lambda^2)$.

	x	y	z	B_{eq} or $B(\text{\AA}^2)$
Br	-1772.0 (5)	5705.2 (4)	3253.7 (4)	9.06 (3)
O(1)	4773 (2)	5992 (1)	5749 (2)	5.0 (1)
O(2)	3985 (3)	7059 (2)	6392 (2)	7.0 (1)
N(1)	8185 (3)	6097 (2)	7223 (2)	4.9 (1)
N(2)	8784 (3)	5801 (2)	8017 (2)	5.5 (2)
C(1)	6790 (4)	5865 (2)	6919 (2)	4.9 (2)
C(2)	6110 (4)	6277 (2)	6163 (2)	5.1 (2)
C(3)	6218 (3)	5201 (2)	7406 (2)	4.6 (2)
C(4)	6714 (4)	4422 (2)	7398 (3)	5.9 (2)
C(5)	6156 (4)	3810 (2)	7837 (3)	6.7 (2)
C(6)	5148 (4)	3974 (2)	8278 (3)	6.2 (2)
C(7)	4693 (4)	4753 (2)	8303 (3)	6.1 (2)
C(8)	5214 (4)	5373 (2)	7861 (2)	5.2 (2)
C(9)	6533 (4)	6958 (2)	5642 (3)	5.1 (2)
C(10)	7367 (4)	7570 (2)	6129 (3)	5.6 (2)
C(11)	7725 (4)	8206 (2)	5612 (3)	6.7 (2)
C(12)	7254 (4)	8212 (3)	4632 (3)	7.5 (3)
C(13)	6448 (4)	7608 (3)	4140 (3)	7.5 (3)
C(14)	6079 (4)	6968 (2)	4646 (3)	6.1 (2)
C(15)	10193 (4)	6045 (2)	8326 (2)	5.4 (2)
C(16)	10881 (4)	5703 (3)	9185 (3)	8.1 (3)
C(17)	12231 (4)	5916 (3)	9572 (3)	9.1 (3)
C(18)	12832 (4)	6435 (3)	9104 (3)	8.7 (3)
C(19)	12178 (4)	6744 (3)	8251 (3)	8.9 (3)
C(20)	10805 (4)	6557 (3)	7839 (3)	7.4 (2)
C(21)	3764 (4)	6496 (2)	5861 (2)	5.2 (2)
C(22)	2421 (3)	6257 (2)	5254 (2)	4.7 (2)
C(23)	2211 (4)	5528 (2)	4788 (2)	5.3 (2)
C(24)	953 (4)	5344 (2)	4211 (3)	6.0 (2)
C(25)	-39 (4)	5915 (2)	4096 (2)	6.2 (2)
C(26)	126 (4)	6649 (3)	4577 (3)	7.6 (3)
C(27)	1394 (4)	6818 (2)	5172 (3)	7.0 (2)
H(4)	752 (4)	432 (2)	707 (3)	9 (1)
H(5)	646 (3)	320 (2)	778 (2)	7 (1)
H(6)	473 (4)	350 (2)	854 (2)	8 (1)
H(7)	401 (3)	483 (2)	871 (2)	6 (1)
H(8)	480 (3)	591 (2)	788 (2)	6 (1)
H(10)	759 (4)	756 (2)	683 (3)	9 (1)
H(11)	827 (4)	874 (2)	602 (3)	9 (1)
H(12)	752 (3)	865 (2)	428 (3)	8 (1)
H(13)	629 (4)	757 (2)	339 (3)	9 (1)
H(14)	536 (3)	647 (2)	434 (2)	7 (1)
H(16)	1030 (4)	541 (2)	954 (3)	11 (2)
H(17)	1269 (4)	548 (3)	1012 (3)	12 (2)
H(18)	1392 (4)	660 (2)	929 (3)	9 (1)
H(19)	1256 (4)	718 (2)	780 (3)	9 (1)
H(20)	1025 (4)	684 (2)	726 (3)	9 (1)
H(23)	300 (3)	514 (2)	487 (2)	7 (1)
H(24)	88 (4)	475 (2)	379 (3)	8 (1)
H(26)	-67 (4)	715 (2)	439 (3)	10 (1)
H(27)	162 (4)	735 (2)	554 (3)	9 (1)

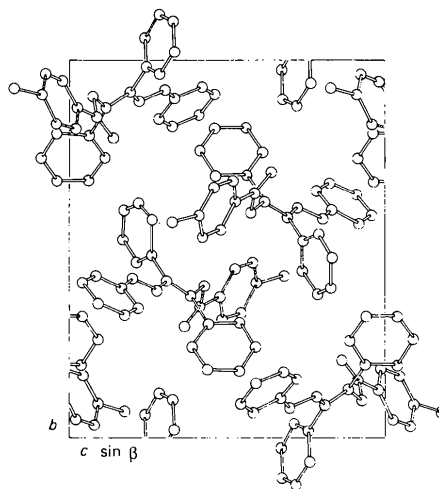


Fig. 2. Unit-cell contents. H atoms have been omitted for clarity.

Table 2. Bond distances (\AA)

Br—C(25)	1.912 (4)	C(12)—C(13)	1.377 (6)
N(1)—N(2)	1.262 (4)	C(13)—C(14)	1.397 (6)
N(1)—C(1)	1.433 (5)	C(14)—C(9)	1.405 (5)
C(1)—C(2)	1.332 (5)	N(2)—C(15)	1.451 (5)
C(2)—O(1)	1.426 (4)	C(15)—C(16)	1.391 (5)
O(1)—C(21)	1.368 (4)	C(16)—C(17)	1.397 (6)
C(21)—O(2)	1.197 (4)	C(17)—C(18)	1.339 (7)
C(1)—C(3)	1.505 (5)	C(18)—C(19)	1.352 (7)
C(3)—C(4)	1.389 (5)	C(19)—C(20)	1.412 (6)
C(4)—C(5)	1.396 (5)	C(20)—C(15)	1.357 (6)
C(5)—C(6)	1.371 (6)	C(21)—C(22)	1.485 (5)
C(6)—C(7)	1.377 (6)	C(22)—C(23)	1.377 (5)
C(7)—C(8)	1.387 (5)	C(23)—C(24)	1.379 (5)
C(8)—C(3)	1.383 (5)	C(24)—C(25)	1.365 (6)
C(2)—C(9)	1.485 (5)	C(25)—C(26)	1.394 (6)
C(9)—C(10)	1.398 (5)	C(26)—C(27)	1.392 (6)
C(10)—C(11)	1.397 (5)	C(27)—C(22)	1.384 (5)
C(11)—C(12)	1.385 (6)		

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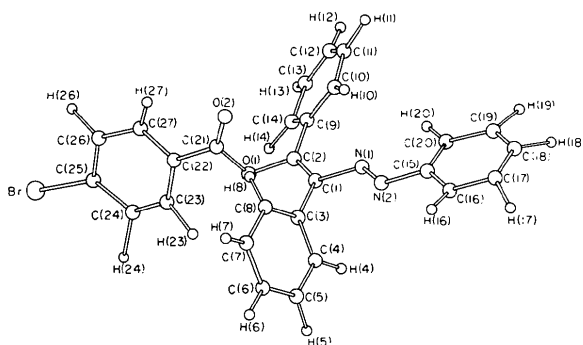


Fig. 1. Structure of $C_{27}H_{19}BrN_2O_2$.