methylation at N(3) is to lengthen the bonds about N(3) (Table 3) compared to those observed in milrinone [1·359 (2) and 1·371 (2) Å for C(2)—N(3) and N(3)—C(4), respectively] (Cody, 1987). There is also a shortening of the 2-methyl bond length in (II), not observed in (I) or milrinone.

In both reported structures the pyridine ring C—N bond lengths are shortened (average 1·33 Å) compared to the C—N values in the pyridone ring (average 1·38 Å). This shortening is also observed in the structures of milrinone and amrinone (Cody, 1987). In (II) the C(3)'—N(4)'—C(5)' angle is significantly larger than in (I) or milrinone free base (Cody, 1987), suggesting that it is a site of protonation of this salt. The pyridinium ring angles of (II) at C(1)', C(3)' and C(5)' are also significantly different than those of (I) (Table 3). These differences are indicative of the positive charge of the pyridinium ring of the salt (II).

There are no hydrogen-bonding functions in (I), and as illustrated in Fig. 2, there is stacking of the pyridone rings (C···C 3·4 Å). There is a network of hydrogen bonds in the hydrobromide hydrate structure (II) (Fig. 3). The water molecules are involved in a series of hydrogen bonds with the bromide ion and the cyano nitrogen (Table 4). The pyridinium nitrogen forms a hydrogen bond with one of the disordered water molecules, and is also involved in a close van der Waals contact (3·41 Å) with the keto oxygen of a neighboring molecule (Fig. 3).

That the free base of (I) has a larger torsion angle between rings than the HBr salt (II), in contrast to that observed for milrinone (Cody, 1987) and its HCl salt (Robertson *et al.*, 1986), appears to be an effect of hydrogen bonds involving the pyridone ring N—H group in both milrinone structures which are not observed for the methylated analogues reported here.

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# Structure of Benzil Benzoylphenylhydrazone

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**Abstract.** 2'-($\alpha$-Benzoylbenzylidene)-1'-phenylbenzohydrazide, $C_{27}H_{20}N_2O_2$, $M_r = 404·47$, orthorhombic, $P2_12_12_1$, $a = 5·742$ (2), $b = 17·383$ (4), $c = 21·487$ (4) Å, $V = 2145$ (5) Å$^3$, $Z = 4$, $D_x = 1·252$ g cm$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu = 5·97$ cm$^{-1}$, $F(000) = 848$, $T = 293$ K, final $wR = 0·043$ for 1465 reflections with $|F_o| > 3\sigma$. This compound is the product of the thermal rearrangement of $\alpha$-benzoyloxy-$\beta$-phenylazostilbene. The structure is the one predicted by a cyclic intermediate or transition state with the $C_6H_5C$=O group rotated away from the migration terminus.

**Introduction.** $\alpha$-Benzoyloxy-$\beta$-phenylazostilbene (I*a*) rearranges on heating, in solution, in the melt or in the solid state, to form benzil benzoylphenylhydrazone (III*a*) as the sole product (Russell & Weisleder, 1967). Kinetic studies in decalin solution showed that

the reaction is first order and remarkably insensitive to substituents in the migrating acyl group (Russell, Strothkamp & Kasprisin, 1969). It was proposed that (I) is a *trans* stilbene and that the rate-determining step of the reaction is an isomerization around —C=C— to the *cis* form, bringing the —C=O and the —N=N— groups closer together, followed by a rapid intramolecular shift to form (II). The rearrangement might occur during the *trans* to *cis* conversion, before the *cis* isomer is actually formed. Pendergrass, Curtin & Paul (1972) corroborated this hypothesis using X-ray crystallographic analysis for an analogous rearrangement.

(Ia) X = H
(Ib) X = Br

(II)    (III)
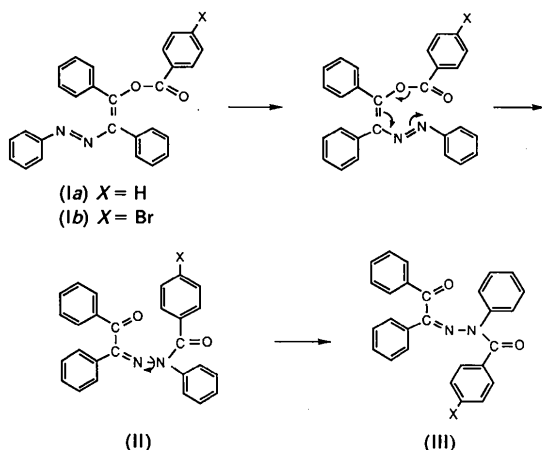
The structure of (Ib) was determined by Bray, Minadeo & Russell (1983) and shown to have the *trans* configuration around the stilbene double bond and around the azo double bond. Cross-over experiments with deuterium-labelled (Ia) ($C_6D_5C=O$) and $^{15}$N-labelled (Ia) ($C_6H_5—^{15}N=$) and mass spectral analyses of the isotopic distribution in the rearrangement products showed that the reaction in solution, solid state or melt is intramolecular (Russell, 1987). These results suggest a six-member cyclic transition state for the rearrangement with the ester oxygen out of the plane. The *trans* configuration at the azo bond is a favorable geometry for this proposed intermediate because it relieves crowding.

If (II) is the intermediate, then the product, (III), will have the *cis* configuration around the —C=N— bond, that is, $C_6H_5C(=O)NC_6H_5$ will be *cis* to $C_6H_5C=O$ and *trans* to $C_6H_5$. The $C_6H_5C(=O)$-$NC_6H_5$ group can rotate around the =N—N bond so that the least crowded conformation or the one giving the best packing in the crystal will result, but the geometry at —C=N— will be dictated by the cyclic nature of the intermediate. This supposition is supported by the structure of (IIIa), which has been determined crystallographically and is presented in this paper.

Table 1. *Fractional coordinates and equivalent isotropic temperature factors for non-H atoms with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | x | y | z | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| O(1) | 1·3363 (4) | 0·0355 (1) | −0·0862 (1) | 3·93 (4) |
| O(2) | 0·7377 (6) | −0·1163 (1) | −0·2324 (1) | 7·21 (8) |
| N(1) | 0·8541 (5) | −0·0465 (1) | −0·0859 (1) | 2·74 (5) |
| N(2) | 0·8878 (5) | −0·0527 (1) | −0·1498 (1) | 3·09 (5) |
| C(1) | 0·9558 (5) | 0·0066 (1) | −0·0541 (1) | 2·45 (5) |
| C(2) | 1·1417 (5) | 0·0619 (2) | −0·0764 (1) | 2·71 (6) |
| C(3) | 0·8974 (5) | 0·0083 (1) | 0·0132 (1) | 2·55 (6) |
| C(4) | 0·6895 (6) | −0·0243 (2) | 0·0345 (1) | 3·28 (6) |
| C(5) | 0·6371 (6) | −0·0237 (2) | 0·0972 (1) | 3·68 (7) |
| C(6) | 0·7892 (7) | 0·0098 (2) | 0·1395 (1) | 3·95 (7) |
| C(7) | 0·9952 (7) | 0·0424 (2) | 0·1186 (1) | 3·82 (7) |
| C(8) | 1·0498 (6) | 0·0419 (2) | 0·0555 (1) | 3·31 (6) |
| C(9) | 1·0902 (6) | 0·1452 (2) | −0·0824 (1) | 2·77 (6) |
| C(10) | 1·2503 (6) | 0·1916 (2) | −0·1125 (2) | 4·02 (7) |
| C(11) | 1·2047 (7) | 0·2691 (2) | −0·1216 (2) | 5·26 (9) |
| C(12) | 1·0017 (8) | 0·3000 (2) | −0·0986 (2) | 5·33 (9) |
| C(13) | 0·8407 (7) | 0·2546 (2) | −0·0678 (2) | 4·65 (8) |
| C(14) | 0·8829 (6) | 0·1770 (2) | −0·0605 (1) | 3·43 (7) |
| C(15) | 0·9360 (6) | 0·0133 (2) | −0·1890 (1) | 3·02 (6) |
| C(16) | 1·1408 (6) | 0·0159 (2) | −0·2229 (1) | 3·60 (7) |
| C(17) | 1·1839 (7) | 0·0797 (2) | −0·2600 (1) | 4·13 (8) |
| C(18) | 1·0249 (8) | 0·1390 (2) | −0·2626 (1) | 4·59 (8) |
| C(19) | 0·8212 (7) | 0·1352 (2) | −0·2291 (1) | 4·10 (8) |
| C(20) | 0·7740 (6) | 0·0716 (2) | −0·1919 (1) | 3·38 (6) |
| C(21) | 0·7831 (7) | −0·1162 (2) | −0·1772 (1) | 4·02 (7) |
| C(22) | 0·7357 (7) | −0·1853 (2) | −0·1374 (1) | 3·63 (7) |
| C(23) | 0·5374 (7) | −0·2271 (2) | −0·1504 (2) | 4·64 (8) |
| C(24) | 0·4893 (8) | −0·2940 (2) | −0·1182 (2) | 5·50 (9) |
| C(25) | 0·6415 (8) | −0·3198 (2) | −0·0737 (2) | 5·56 (9) |
| C(26) | 0·8421 (8) | −0·2794 (2) | −0·0609 (2) | 5·26 (9) |
| C(27) | 0·8903 (7) | −0·2108 (2) | −0·0927 (1) | 4·22 (8) |
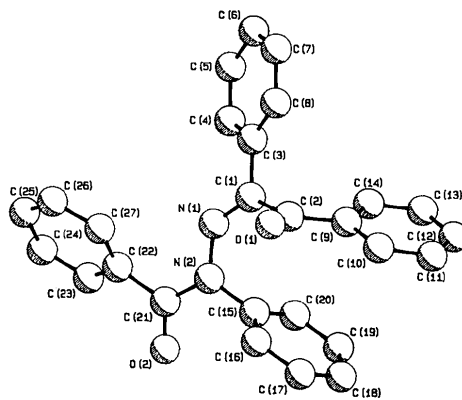


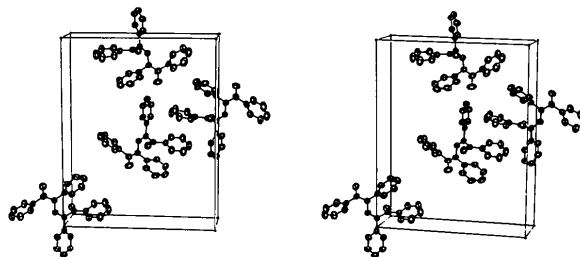Fig. 1. Structure of the molecule with numbering scheme for the non-H atoms.



Fig. 2. Stereoview of the unit cell with thermal ellipsoids at 59% probability.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

| | | | | | | |
|---|---|---|---|---|---|---|
| O(1) | C(2) | 1·226 (4) | C(10) | C(11) | 1·385 (4) | |
| O(2) | C(2) | 1·214 (3) | C(11) | C(12) | 1·375 (6) | |
| N(1) | N(2) | 1·392 (3) | C(12) | C(13) | 1·384 (5) | |
| N(1) | C(1) | 1·288 (3) | C(13) | C(14) | 1·381 (4) | |
| N(2) | C(15) | 1·450 (3) | C(15) | C(16) | 1·385 (5) | |
| N(2) | C(21) | 1·388 (4) | C(15) | C(20) | 1·376 (4) | |
| C(1) | C(2) | 1·515 (4) | C(16) | C(17) | 1·389 (4) | |
| C(1) | C(3) | 1·484 (4) | C(17) | C(18) | 1·378 (5) | |
| C(2) | C(9) | 1·483 (4) | C(18) | C(19) | 1·376 (5) | |
| C(3) | C(4) | 1·399 (4) | C(19) | C(20) | 1·392 (4) | |
| C(3) | C(8) | 1·390 (4) | C(21) | C(22) | 1·498 (4) | |
| C(4) | C(5) | 1·381 (4) | C(22) | C(23) | 1·379 (5) | |
| C(5) | C(6) | 1·388 (5) | C(22) | C(27) | 1·382 (5) | |
| C(6) | C(7) | 1·385 (5) | C(23) | C(24) | 1·382 (5) | |
| C(7) | C(8) | 1·392 (4) | C(24) | C(25) | 1·371 (6) | |
| C(9) | C(10) | 1·384 (4) | C(25) | C(26) | 1·376 (6) | |
| C(9) | C(14) | 1·394 (4) | C(26) | C(27) | 1·402 (4) | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(2) | N(1) | C(1) | 121·0 (2) | C(11) | C(12) | C(13) | 121·0 (3) |
| N(1) | N(2) | C(15) | 122·6 (2) | C(12) | C(13) | C(14) | 119·6 (3) |
| N(1) | N(2) | C(21) | 114·8 (2) | C(9) | C(14) | C(13) | 120·0 (3) |
| C(15) | N(2) | C(21) | 117·8 (2) | N(2) | C(15) | C(16) | 119·5 (3) |
| N(1) | C(1) | C(2) | 127·4 (2) | N(2) | C(15) | C(20) | 118·7 (3) |
| N(1) | C(1) | C(3) | 115·4 (2) | C(16) | C(15) | C(20) | 121·8 (3) |
| C(2) | C(1) | C(3) | 117·0 (2) | C(15) | C(16) | C(17) | 118·6 (3) |
| O(1) | C(2) | C(1) | 117·3 (2) | C(16) | C(17) | C(18) | 120·2 (3) |
| O(1) | C(2) | C(9) | 122·2 (3) | C(17) | C(18) | C(19) | 120·4 (3) |
| C(1) | C(2) | C(9) | 120·4 (3) | C(18) | C(19) | C(20) | 120·3 (3) |
| C(1) | C(3) | C(4) | 120·2 (2) | C(15) | C(20) | C(19) | 118·6 (3) |
| C(1) | C(3) | C(8) | 120·2 (3) | O(2) | C(21) | N(2) | 120·5 (3) |
| C(4) | C(3) | C(8) | 119·6 (2) | O(2) | C(21) | C(22) | 121·1 (3) |
| C(3) | C(4) | C(5) | 120·2 (3) | N(2) | C(21) | C(22) | 118·3 (2) |
| C(4) | C(5) | C(6) | 120·2 (3) | C(21) | C(22) | C(23) | 117·2 (3) |
| C(5) | C(6) | C(7) | 119·9 (3) | C(21) | C(22) | C(27) | 122·5 (3) |
| C(6) | C(7) | C(8) | 120·3 (3) | C(23) | C(22) | C(27) | 120·1 (3) |
| C(3) | C(8) | C(7) | 119·8 (3) | C(22) | C(23) | C(24) | 120·5 (3) |
| C(2) | C(9) | C(10) | 118·5 (3) | C(23) | C(24) | C(25) | 119·8 (4) |
| C(2) | C(9) | C(14) | 121·8 (3) | C(24) | C(25) | C(26) | 120·4 (3) |
| C(10) | C(9) | C(14) | 119·6 (3) | C(25) | C(26) | C(27) | 120·1 (3) |
| C(9) | C(10) | C(11) | 120·5 (3) | C(22) | C(27) | C(26) | 119·0 (3) |
| C(10) | C(11) | C(12) | 119·3 (3) | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C(1) | N(1) | N(2) | C(15) | −30·2 (4) | C(1) | N(1) | N(2) | C(21) | 174·9 (3) |
| N(2) | N(1) | C(1) | C(2) | −8·1 (4) | N(2) | N(1) | C(1) | C(3) | 177·8 (2) |
| N(1) | N(2) | C(21) | O(2) | 157·3 (3) | N(1) | N(2) | C(21) | C(22) | −24·8 (4) |
| C(15) | N(2) | C(21) | O(2) | 1·2 (5) | C(15) | N(2) | C(21) | C(22) | 179·1 (3) |
| N(1) | C(1) | C(2) | O(1) | −71·5 (4) | N(1) | C(1) | C(2) | C(9) | 111·9 (3) |
| C(3) | C(1) | C(2) | O(1) | 102·6 (3) | C(3) | C(1) | C(2) | C(9) | −74·1 (3) |

**Experimental.** Suitable crystals of the title compound were obtained as the reaction product from the melt; no further purification was necessary. Crystal dimensions $0.15 \times 0.20 \times 0.30$ mm, Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Cell parameters from 25 reflections in the $2\theta$ range 20–40°. Range of indices $0 \le h \le 6$, $0 \le k \le 19$, $0 \le l \le 24$ ($\theta < 60°$). Three standards measured after every 200 reflections showed a variation of 0·3%. Lorentz–polarization correction, no absorption correction. 1881 unique ($R_{int} = 0.013$) reflections measured; 1465 observed reflections with $|F_o| > 3\sigma(|F_o|)$. Direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) were used for structure determination. Calculated positions for H atoms initially used. Anisotropic full-matrix least-squares refinement (on $F$) for non-H atoms; two cycles of isotropic refinement on H atoms, fixed positions in subsequent cycles, $B_{iso}$ for H atoms fixed at 5·0 Å². $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 4F_o^2/S^2(I)$, $S(I) = [\sigma^2(I) + p(F_o)^2]^{1/2}$, $p =$

0·04. $R = 0.035$, $wR = 0.043$, max. $\Delta/\sigma = 0.07$, $S = 1.37$ for 281 variables, maximum and minimum peak heights in final difference map 0·31 and $-0.33$ e Å$^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All programs in Enraf–Nonius *SDP* (Frenz, 1983). Atomic parameters are given in Table 1,* bond distances, bond angles and relevant torsion angles are in Table 2.

**Discussion.** The structure of (IIIa) is shown in Fig. 1 and is the one predicted by the cyclic intermediate or transition state, (II). $C_6H_5C\!\!=\!\!O$ is rotated away from the migration terminus possibly to avoid steric hindrance and electronic repulsion between the two carbonyl groups. This is suggested further by the large N(1)—C(1)—C(2) angle of 127·4 (2)° and also the N(1)—N(2)—C(15) angle of 122·6 (2)°. The distance of 1·515 (4) Å between C(1) and C(2) shows that C=N and C=O are not conjugated with each other. This is confirmed by the torsion angle N(1)—C(1)—C(2)—O(1) of $-71.5$ (4)°. Although the shorter length of 1·388 (4) Å between N(2) and C(21) in the amide group indicates some double-bond character, the bonds around N(2) are not strictly planar. A stereoview (Johnson, 1965) is shown in Fig. 2.

* 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 53144 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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