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# X-ray analysis and spectral data of β-[N-phenyl,N-(β′-bromo-cinnamoyl)-amino]-cinnamanilide reveal the course of reaction of benzoylacetanilide with $POBr_3$

**M. Ciechanowicz-Rutkowska,[1] P. Serda,[1] B. Stec,*,[1] and A. Kolasa[2]**

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The reaction of benzoylacetanilide with the excess of $POBr_3$ furnished monomolecular products and the bimolecular β-[N-phenyl,N-(β-bromo-cinnamoyl)-amino]-cinnamanilide. Its structure was elucidated by means of elemental analysis, IR, $^1H$ NMR and mass spectral data as well as X-ray analysis, which proved that the reaction mentioned goes via condensation. $C_{30}H_{23}BrN_2O_2$ crystallizes with two independent molecules in an asymmetric unit in the orthorhombic space group $P2_12_12_1$ with $a_3 = 9.834(3)$, $b = 19.614(2)$, $c = 26.450(6)$ Å, $Z = 8$, $V = 5101(4)$ Å$^3$, $D_m = 1.34$, $D_x = 1.36$ mg m$^{-3}$, F(000) = 2151, $M_r = 523.107$, $\mu = 2.25$ mm$^{-1}$, λ (Cu $K\alpha$) = 1.54178 Å, $T = 293$ K; the final $R$ factor was 0.067.

## Introduction

The model of reactivity of benzoylacetanilides in the presence of the excess of $POX_3$ ($X$ = Cl, Br) on heating is a subject of interest since the compound is a parent for the new derivatives of natural truxinic acid. The reaction of benzoylacetanilide with $POCl_3$, via "head to head" cycloaddition accompanied by substitution of HO group for Cl, leads to 3,4-diphenyl-3,4-dichloro-cyclobutanodicarbox-1,2-dianilide in the form of its β-stereoisomer (Ciechanowicz-Rutkowska *et al.*, 1981). This process cannot be treated as a good synthetical method because the yield of this bimolecular products is relatively low since a mixture of HO- and Cl-substituted quinolines is also obtained. However, the product mentioned seemed to be so interesting and its separation from the reaction mixture relatively easy, that we decided to extend the range of this reaction to $POBr_3$. Surprisingly, the main bimolecular product of the reaction of benzoylacetanilide with the excess of $POBr_3$ differs analytically from the analogous Cl-substituted derivatives by HBr. Complexity of its spectroscopic data, showing many nonequivalent functional groups, did not allow to elucidate the structure unambiguosly and X-ray method was necessary to prove the cyclobutene or open structure and to distinguish among a wide variety of possible stereoisomers (Fig. 1).

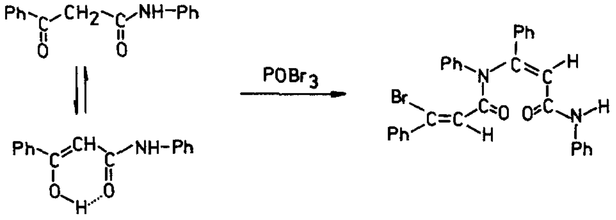

**Fig. 1.** Course of the reaction of benzoylacetanilide with the excess of $POBr_3$.

## Experimental

The following physicochemical studies were carried out. The melting point was measured but not corrected. The IR spectrum was taken in Nujol (600–2000 cm$^{-1}$) and hexachlorobutadiene (2000–4000 cm$^{-1}$) on a Specord IR 75 apparatus. $^1H$ NMR spectrum was recorded in $CDCl_3$ with TMS as internal standard on

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[1] Regional Laboratory of Physicochemical Analysis and Structural Research, Karasia 3, 30-060 Kraków, Poland.

[2] Faculty of Chemistry, Jagiellonian University, Karasia 3, 30-060 Kraków, Poland.

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Jeol 100 MHz apparatus. The mass spectrum was measured at 20 eV on an LKB 9000 S spectrometer in the Regional Laboratory of Physicochemical Analysis and Structural Research in Cracow.

### β-[N-phenyl,N-(β′-bromo-cinnamoyl)-amino]-cinnamanilide

A mixture of benzoylacetanilide (23.9 g, 0.1 mole) and $POBr_3$ (239.0 g, 0.8 mole) was heated on a steam bath for 15 min. The solution was then poured into icy water and the crude reaction mixture was filtered off, dried, and dissolved in 200 ccm of cold ethanol. After a few hours the precipitate of the product was filtered off (3.2 g, 12.2% yield) and crystallized from chloroform. Colorless needles, m.p. : 211°C with decomposition.

Analysis for $C_{30}H_{23}BrN_2O_2$: calc.: 68.8% C, 4.4% H, 5.3% N, 15.3% Br, found: 68.3% C, 4.5% H, 5.0% N, 15.4% Br.

*Spectral data*

IR [$cm^{-1}$]:

| | |
|---|---|
| 3305 m<br>3250 m<br>3180 w<br>3120 w | ν N−H, bonded |
| 3080 w | ν C−H, aromat. |
| 1680 s<br>1640 s | ν C=O, |
| 1620 s<br>1600 s<br>1550 s | ν C=C, |

$^1H$ NMR δ[ppm]: 6.62, s, 1 H, −CH=
6.76, s, 1 H, −CH=
7.0 − 7.7, m, 20 H, aromat.
(NH signal not identified)

MS [m/z (% intensity)]: 522(40.0) $M^+$, 442(49.5) $M^+$ − HBr, 402(22.1) $M^+$ − PhNHCO, 399(16.8), 350(36.8) $M^+$ − HBr, − PhNH, 323(66.3) $M^+$ − PhNHCO, − HBr, 294(28.4), 169(32.6), 234(32.6), 222(100.0) $PhNHCOCH{=}CHPh^+$, 209(23.2) $PhCBr{=}CH{-}C{\equiv}O^+$, 193(24.2) $PhC(NPh){=}CH^+$, 180(45.3) $PhC{\equiv}N^+{-}Ph$, 129(15.8) $PhC{\equiv}{=}C{-}C{\equiv}O^+$, 119(49.5) $PhNCO^+$, 105(18.9), 93(32.6), 91(24.2), 80(28.4) $HBr^+$, 64(11.6) $C_2H_2^+$.

A crystal suitable for single crystal X-ray diffraction was obtained by crystallization from acetic acid. The details of data collection and structure refinement are given in Table 1.

The structure was solved in $P2_12_12_1$ space group by direct methods using SHELXS86 (Sheldrick, 1986). All nonhydrogen atoms were revealed in an E-map based on 388 reflections with E ≥ 1.2 and three nonphenyl hydrogens of the backbone of the molecule were located in a subsequent difference Fourier map and refined. Hydrogens of phenyl rings with calculated coordinates were included in the refinement as fixed contribution because of the large number of atoms (70) and refined parameters (656). The refinement was carried out with SHELX76 (400-atomic version) on the data corrected for absorption, the crystal faces being refined by Miller indices and distances from a common reference point inside the crystal. The structure of one of the two independent molecules (molecule A) is depicted together with the atom labeling scheme in Fig. 2. Tables 2 and 3 list the coordinates and thermal parameters for the heavy atoms. In Table 4 hydrogen coordinates are listed. The total difference Fourier map has revealed peaks in the vicinity of bromine atoms not higher than one electron probably due to the series termination effects.

## Discussion

X-ray analysis has shown that there are two independent β-[N-phenyl,N-(β′-bromo-cinnamoyl)-amino]-cinnamanilide molecules in the unit cell. They are illustrated in Fig. 3 together with the phenyl ring numbering scheme. Despite poor quality of the crystal and, in consequence, high *R* factor we have obtained a relatively good structure with well defined features. Bond lengths and selected bond angles and torsion angles listed in Tables 5, 6, 7 have the commonly accepted values, and in particular the C−Br bond length is comparable with that found in bromo-dioxane derivative (Żmudzinski *et*

**Table 1.** Crystal data and summary of data collection and structure refinement

| | |
|---|---|
| Molecular formula | $C_{30}H_{23}BrN_2O_2$ |
| Molecular weight | 523.107 |
| Crystal system | orthorhombic |
| Space group, $Z$ | $P2_12_12_1$, 8 |
| $a$, $b$, $c$/Å | 9.834(3), 19.614(2), 26.450(6) |
| $D_m$, $D_x$/gm cm$^{-3}$ | 1.34(2), 1.362(1) |
| Radiation | CuK$\alpha$, $\lambda$ = 1.54178 Å |
| $\mu$(Cu $K\alpha$) | 2.25 mm$^{-1}$ |
| Crystal shape and size (mm) | Colorless prisms (011)<br>0.20 × 0.11 × 0.14 |
| Measuring $D_m$ | Flotation in KJ aq. solution |
| Diffractometer | Enraf-Nonius CAD-4 (graphite-monochromated Cu $K\alpha$ radiation) |
| Lattice-parameter measurement | |
| $\theta$ range, number of relections | $8 \le \theta \le 18°$, 25 |
| Intensity measurement: | |
| $\theta$ range | $1 \le \theta \le 71°$ |
| Indices range | $-12 \le h \le 0$, $-24 \le k \le 24$, $0 \le l \le 32$ |
| Scan width (°) and mode | $0.50 + 0.15 \tan \theta$, $\omega/2\theta$ |
| Intensity control reflections | 213,222 measured every hour |
| Changes in intensity | <3% |
| Number of reflections measured | 6695 |
| Criterion for observed refl. | $\lvert F_o \rvert \ge 3\sigma(F)$ |
| Number of observed unique refl. | 6249 |
| Corrections applied | Lorentz, polarization, absorption |
| Transmission factors | 0.64, 0.77 |
| Extinction reflections omitted | 110, 012 |
| Refinement method | Full-matrix LSQ on $\lvert F_o \rvert$ |
| Parameters refined | 656 |
| Non-H-atoms | Positional and anis. thermal |
| H-atoms[a] | Positional and isotr. thermal |
| Weighting scheme $k$ and $g$ | $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ |
| converged to | 2.538, 0.00073 |
| $R$, $wR$, $S$ | 0.0671, 0.0876, 2.735 |
| Average, max. $\Delta/\sigma$ | 0.05, 0.11 |
| Max., min. height in final difference Fourier map (e Å$^{-3}$) | 1.1, −1.34 |

[a] Initial positional H-atom parameters for phenyls in calculated positions; others from the difference Fourier maps.

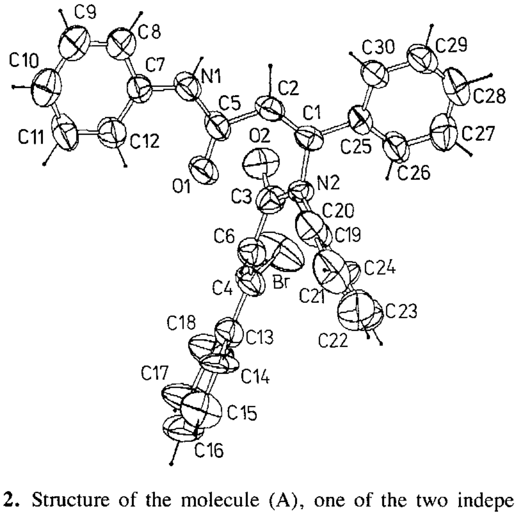

**Fig. 2.** Structure of the molecule (A), one of the two independent molecules, with hydrogens and atom labelling scheme. Hydrogen numbers are the same as those of the heavy atoms bonded to them. Thermal ellipsoid vibrations are scaled to enclose 50% probability.

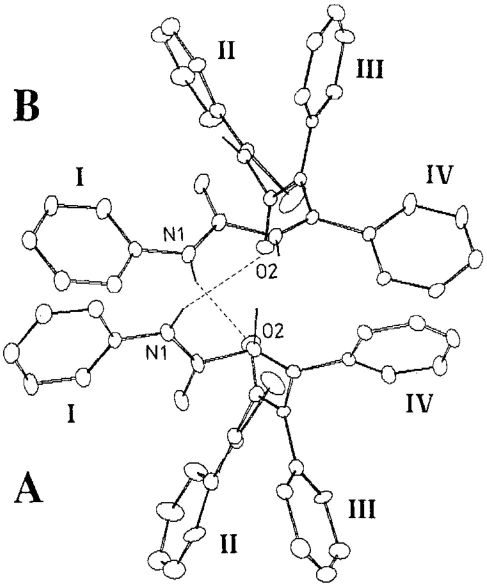

**Fig. 3.** Asymmetric part of the unit cell shows a dimer with hydrogen bonds N1A—H1A · · · O2B, N1B—H1B · · · O2B. Thermal ellipsoids correspond to 10% probability.

**Table 2.** Coordinates of heavy atoms with esd's in parentheses

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ | Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| N1A | 1.3408(5) | 0.4677(3) | 0.1857(2) | 594(8) | N1B | 0.8436(5) | 0.5646(2) | 0.1796(2) | 594(9) |
| N2A | 1.0671(4) | 0.3678(2) | 0.0820(2) | 430(9) | N2B | 0.5652(4) | 0.6553(2) | 0.0785(2) | 406(9) |
| O1A | 1.1845(5) | 0.3818(2) | 0.1778(2) | 822(8) | O1B | 0.6990(5) | 0.6516(3) | 0.1699(2) | 833(9) |
| O2A | 0.9426(4) | 0.4519(2) | 0.1163(2) | 693(9) | O2B | 0.4524(4) | 0.5708(2) | 0.1174(2) | 631(9) |
| C1A | 1.1727(5) | 0.4161(3) | 0.0682(2) | 469(9) | C1B | 0.6691(5) | 0.6075(3) | 0.0638(2) | 455(9) |
| C2A | 1.2499(6) | 0.4462(3) | 0.1037(2) | 586(10) | C2B | 0.7545(6) | 0.5858(3) | 0.0979(2) | 578(9) |
| C3A | 0.9641(6) | 0.3904(3) | 0.1106(2) | 559(9) | C3B | 0.4675(5) | 0.6324(3) | 0.1112(2) | 478(8) |
| C4A | 0.7451(6) | 0.3347(4) | 0.1392(2) | 674(9) | C4B | 0.2537(6) | 0.6892(3) | 0.1402(2) | 583(9) |
| C5A | 1.2519(6) | 0.4280(4) | 0.1591(2) | 641(10) | C5B | 0.7610(6) | 0.6033(3) | 0.1517(2) | 536(9) |
| C6A | 0.8807(6) | 0.3376(3) | 0.1362(2) | 565(10) | C6B | 0.3871(5) | 0.6831(3) | 0.1386(2) | 492(9) |
| BR1A | 0.6392(1) | 0.4035(1) | 0.1057(0) | 1174(4) | BR1B | 0.1490(1) | 0.6302(1) | 0.1003(1) | 1453(4) |
| C7A | 1.3870(6) | 0.4584(3) | 0.2350(2) | 525(9) | C7B | 0.8828(6) | 0.5703(3) | 0.2301(2) | 545(9) |
| C8A | 1.4974(7) | 0.4969(3) | 0.2500(3) | 705(10) | C8B | 0.8329(7) | 0.6190(4) | 0.2615(2) | 775(10) |
| C9A | 1.5494(8) | 0.4899(4) | 0.2970(3) | 865(10) | C9B | 0.8809(8) | 0.6223(4) | 0.3115(2) | 805(10) |
| C10A | 1.4988(7) | 0.4436(4) | 0.3293(3) | 816(10) | C10B | 0.9746(8) | 0.5807(4) | 0.3288(2) | 822(10) |
| C11A | 1.3901(8) | 0.4045(4) | 0.3157(3) | 809(10) | C11B | 1.0273(8) | 0.5312(4) | 0.2965(3) | 928(10) |
| C12A | 1.3326(7) | 0.4110(4) | 0.2676(2) | 744(10) | C12B | 0.9795(7) | 0.5264(3) | 0.2478(3) | 700(10) |
| C13A | 0.6678(7) | 0.2836(3) | 0.1666(2) | 643(9) | C13B | 0.1798(6) | 0.7415(3) | 0.1702(2) | 583(9) |
| C14A | 0.7462(8) | 0.2156(4) | 0.1814(3) | 1089(9) | C14B | 0.2463(7) | 0.7982(3) | 0.1889(3) | 664(10) |
| C15A | 0.6604(9) | 0.1720(4) | 0.2051(3) | 1042(9) | C15B | 0.1771(8) | 0.8457(4) | 0.2162(3) | 844(10) |
| C16A | 0.5332(8) | 0.1842(4) | 0.2213(3) | 1018(10) | C16B | 0.0424(8) | 0.8355(4) | 0.2288(3) | 969(9) |
| C17A | 0.4717(8) | 0.2454(5) | 0.2129(4) | 1273(10) | C17B | −0.0234(8) | 0.7816(4) | 0.2104(4) | 1327(10) |
| C18A | 0.5398(8) | 0.2934(4) | 0.1853(3) | 984(10) | C18B | 0.0445(7) | 0.7320(4) | 0.1818(4) | 1050(10) |
| C19A | 1.0897(7) | 0.2987(3) | 0.0691(2) | 650(9) | C19B | 0.5811(5) | 0.7264(3) | 0.0658(2) | 446(9) |
| C24A | 1.2125(8) | 0.2691(4) | 0.0759(3) | 799(9) | C20B | 0.4714(6) | 0.7631(3) | 0.0483(2) | 598(10) |
| C23A | 1.2304(10) | 0.2006(4) | 0.0625(3) | 1080(10) | C21B | 0.4867(7) | 0.8314(3) | 0.0370(3) | 816(9) |
| C22A | 1.1309(12) | 0.1666(4) | 0.0419(4) | 1354(10) | C22B | 0.6117(8) | 0.8630(4) | 0.0416(3) | 858(10) |
| C21A | 1.0065(11) | 0.1951(4) | 0.0334(4) | 1209(9) | C23B | 0.7186(7) | 0.8265(3) | 0.0588(3) | 708(10) |
| C20A | 0.9859(8) | 0.2611(3) | 0.0471(3) | 804(10) | C24B | 0.7047(6) | 0.7577(3) | 0.0713(2) | 619(9) |
| C25A | 1.1886(6) | 0.4311(3) | 0.0145(2) | 485(9) | C25B | 0.6705(6) | 0.5867(3) | 0.0097(2) | 471(9) |
| C30A | 1.0892(7) | 0.4124(4) | −0.0204(2) | 679(9) | C26B | 0.6007(6) | 0.6234(4) | −0.0265(3) | 731(10) |
| C29A | 1.1044(7) | 0.4222(4) | −0.0710(3) | 796(10) | C27B | 0.6070(7) | 0.6057(4) | −0.0773(2) | 754(10) |
| C28A | 1.2175(8) | 0.4556(4) | −0.0873(3) | 778(9) | C28B | 0.6791(7) | 0.5540(4) | −0.0925(2) | 735(9) |
| C27A | 1.3170(7) | 0.4757(4) | −0.0548(3) | 730(10) | C29B | 1.2493(7) | 0.0158(3) | 0.5560(3) | 728(10) |
| C26A | 1.3052(6) | 0.4635(3) | −0.0054(2) | 579(9) | C30B | 0.7464(7) | 0.5315(3) | −0.0062(2) | 605(9) |

**Table 3.** Thermal parameters $U_{ij}$ × 10**3: Exp (−2*PI**2(U11*H**2*(A*)**2 + · · · + 2*U12*H*K*(A*)*(B*) + · · ·)

| Atom | *U*11 | *U*22 | *U*33 | *U*23 | *U*13 | *U*12 |
|---|---|---|---|---|---|---|
| N1A | 52(2) | 76(2) | 51(2) | 12(1) | 8(2) | −10(2) |
| N2A | 47(2) | 29(2) | 53(2) | −2(1) | 8(1) | −5(1) |
| O1A | 88(2) | 100(2) | 59(2) | 27(1) | −6(2) | −46(2) |
| O2A | 64(2) | 54(2) | 90(2) | −13(1) | 13(2) | 0(2) |
| C1A | 45(2) | 39(2) | 57(2) | 6(2) | 13(2) | 1(2) |
| C2A | 53(2) | 62(2) | 62(2) | 17(2) | 9(2) | −8(2) |
| C3A | 43(2) | 62(2) | 63(2) | −7(2) | −3(2) | −10(2) |
| C4A | 56(2) | 83(2) | 63(2) | 4(2) | 20(2) | −2(2) |
| C5A | 59(2) | 91(2) | 43(2) | 18(2) | 2(2) | −18(2) |
| C6A | 47(2) | 65(2) | 57(2) | 2(2) | 5(2) | −7(2) |
| BR1A | 62(1) | 138(1) | 153(1) | 71(1) | 3(1) | 2(1) |
| C7A | 48(2) | 58(2) | 52(2) | −1(2) | 3(2) | −5(2) |
| C8A | 79(2) | 73(2) | 59(2) | 0(2) | −4(2) | −4(2) |
| C9A | 85(2) | 84(2) | 91(2) | −5(2) | −27(2) | −21(2) |
| C10A | 75(2) | 112(2) | 59(2) | −11(2) | −20(2) | 0(2) |
| C11A | 89(2) | 95(2) | 58(2) | 15(2) | 5(2) | 0(2) |
| C12A | 62(2) | 103(2) | 59(2) | 6(2) | −(2) | −13(2) |
| C13A | 62(2) | 62(2) | 69(2) | −2(2) | 6(2) | −7(2) |
| C14A | 136(2) | 67(2) | 124(2) | −37(2) | 95(2) | −60(2) |
| C15A | 107(2) | 67(2) | 139(2) | 4(2) | 50(2) | −1(2) |
| C16A | 95(2) | 74(2) | 137(2) | 8(2) | 35(2) | −32(2) |
| C17A | 71(2) | 104(2) | 207(2) | 23(2) | 67(2) | −7(2) |
| C18A | 66(2) | 72(2) | 157(2) | 17(2) | 34(2) | −1(2) |
| C19A | 79(2) | 62(2) | 54(2) | 4(2) | 29(2) | 2(2) |
| C24A | 103(2) | 68(2) | 69(2) | 10(2) | 26(2) | 17(2) |
| C23A | 148(2) | 74(2) | 102(2) | 11(2) | 34(2) | 42(2) |
| C22A | 239(2) | 50(2) | 116(2) | −8(2) | −13(2) | 47(2) |
| C21A | 194(2) | 47(2) | 123(2) | −13(2) | 14(2) | −17(2) |
| C20A | 106(2) | 44(2) | 91(2) | −16(2) | 10(2) | −17(2) |
| C25A | 53(2) | 44(2) | 49(2) | (2) | 15(2) | 13(2) |
| C30A | 61(2) | 87(2) | 56(2) | 7(2) | 9(2) | −11(2) |
| C29A | 71(2) | 106(2) | 62(2) | 2(2) | −9(2) | 6(2) |
| C28A | 92(2) | 86(2) | 56(2) | 16(2) | 18(2) | 28(2) |
| C27A | 76(2) | 80(2) | 62(2) | 12(2) | 32(2) | 2(2) |
| C26A | 64(2) | 56(2) | 55(2) | 3(2) | 16(2) | −6(2) |
| N1B | 62(2) | 58(2) | 59(2) | −12(1) | 0(2) | 21(2) |
| N2B | 35(1) | 43(2) | 43(2) | 1(1) | 5(1) | 4(1) |
| O1B | 81(2) | 110(2) | 59(2) | −27(1) | −14(2) | 47(2) |
| O2B | 57(2) | 57(2) | 75(2) | 4(1) | 25(1) | −6(1) |
| C1B | 37(2) | 50(2) | 50(2) | −7(1) | 8(2) | 3(2) |
| C2B | 54(2) | 70(2) | 49(2) | −4(2) | −10(2) | 26(2) |
| C3B | 40(2) | 52(2) | 51(2) | −2(2) | 9(2) | −9(2) |
| C4B | 47(2) | 76(2) | 51(2) | −9(2) | 10(2) | 9(2) |
| C5B | 40(2) | 63(2) | 58(2) | −12(2) | 1(2) | 19(2) |
| C6B | 44(2) | 48(2) | 56(2) | −7(2) | 15(2) | −7(2) |
| BR1B | 54(1) | 189(1) | 193(1) | −118(1) | −20(1) | 9(1) |
| C7B | 56(2) | 55(2) | 53(2) | −1(2) | 0(2) | 4(2) |
| C8B | 71(2) | 106(2) | 55(2) | −8(2) | −3(2) | 22(2) |
| C9B | 87(2) | 111(2) | 44(2) | −17(2) | 10(2) | 0(2) |
| C10B | 103(2) | 88(2) | 56(2) | 13(2) | −24(2) | 1(2) |
| C11B | 121(2) | 84(2) | 73(2) | 3(2) | −35(2) | 25(2) |
| C12B | 80(2) | 70(2) | 60(2) | −5(2) | −9(2) | 27(2) |
| C13B | 45(2) | 66(2) | 65(2) | 10(2) | 26(2) | 15(2) |

**Table 3.** Continued

| Atom | *U*11 | *U*22 | *U*33 | *U*23 | *U*13 | *U*12 |
|---|---|---|---|---|---|---|
| C14B | 60(2) | 53(2) | 86(2) | −12(2) | 25(2) | 2(2) |
| C15B | 96(2) | 73(2) | 84(2) | −7(2) | 8(2) | −1(2) |
| C16B | 101(2) | 80(2) | 110(2) | −9(2) | 56(2) | 11(2) |
| C17B | 81(2) | 90(2) | 227(2) | −27(2) | 96(2) | 5(2) |
| C18B | 54(2) | 82(2) | 179(2) | −30(2) | 48(2) | −7(2) |
| C19B | 43(2) | 50(2) | 41(2) | −3(2) | 3(2) | −10(2) |
| C20B | 47(2) | 56(2) | 76(2) | 6(2) | 3(2) | −6(2) |
| C21B | 82(2) | 58(2) | 105(2) | 16(2) | −3(2) | 11(2) |
| C22B | 107(2) | 63(2) | 87(2) | 9(2) | 22(2) | −10(2) |
| C23B | 63(2) | 71(2) | 78(2) | −16(2) | 11(2) | −28(2) |
| C24B | 45(2) | 71(2) | 70(2) | −15(2) | 7(2) | −4(2) |
| C25B | 42(2) | 53(2) | 46(2) | −8(2) | 7(2) | −11(2) |
| C26B | 47(2) | 119(2) | 53(2) | −12(2) | −5(2) | 9(2) |
| C27B | 67(2) | 118(2) | 41(2) | −17(2) | −8(2) | 14(2) |
| C28B | 80(2) | 82(2) | 58(2) | −15(2) | 14(2) | −21(2) |
| C29B | 90(2) | 55(2) | 73(2) | 15(2) | 19(2) | −1(2) |
| C30B | 85(2) | 51(2) | 46(2) | 5(2) | 17(2) | 3(2) |

**Table 4.** Coordinates of hydrogen atoms [esd's and thermal parameters omitted for hydrogens in calculated positions (not refined)]

|  | *x* | *y* | *z* | *U* × 10**3 |  | *x* | *y* | *z* | *U* × 10**3 |
|---|---|---|---|---|---|---|---|---|---|
| H1A | 1.401(2) | 0.494(2) | 0.160(1) | 26(2) | H1B | 0.866(2) | 0.525(1) | 0.161(1) | 28(2) |
| H2A | 1.304(2) | 0.495(2) | 0.099(1) | 61(2) | H2B | 0.814(2) | 0.547(1) | 0.089(1) | 34(2) |
| H6A | 0.934(2) | 0.243(2) | 0.150(1) | 61(2) | H6B | 1.447(2) | 0.707(1) | 0.157(1) | 36(2) |
| H8A | 1.5384 | 0.5284 | 0.2254 |  | H8B | 0.7634 | 0.6525 | 0.2495 |  |
| H9A | 1.6275 | 0.5197 | 0.3091 |  | H9B | 0.8401 | 0.6573 | 0.3346 |  |
| H10A | 1.5392 | 0.4384 | 0.3647 |  | H10B | 1.0127 | 0.5871 | 0.3635 |  |
| H11A | 1.3522 | 0.3700 | 0.3408 |  | H11B | 1.1009 | 0.4973 | 0.3089 |  |
| H12A | 1.2561 | 0.3810 | 0.2567 |  | H12B | 1.0137 | 0.4895 | 0.2255 |  |
| H14A | 0.8354 | 0.2081 | 0.1684 |  | H14B | 0.3460 | 0.8047 | 0.1821 |  |
| H15A | 0.7031 | 0.1261 | 0.2139 |  | H15B | 0.2235 | 0.8895 | 0.2272 |  |
| H16A | 0.4823 | 0.1480 | 0.2386 |  | H16B | −0.0049 | 0.8677 | 0.2520 |  |
| H17A | 0.3807 | 0.2568 | 0.2271 |  | H17B | −0.1214 | 0.7762 | 0.2208 |  |
| H18A | 0.4901 | 0.3394 | 0.1748 |  | H18B | −0.0062 | 0.6906 | 0.1682 |  |
| H20A | 1.2901 | 0.2961 | 0.0912 |  | H20B | 0.3819 | 0.7390 | 0.0423 |  |
| H21A | 1.3217 | 0.1751 | 0.0697 |  | H21B | 0.4024 | 0.8597 | 0.0249 |  |
| H22A | 1.1464 | 0.1173 | 0.0315 |  | H22B | 0.6198 | 0.9124 | 0.0321 |  |
| H23A | 0.9315 | 0.1659 | 0.0171 |  | H23B | 0.8093 | 0.8492 | 0.0612 |  |
| H24A | 0.8944 | 0.2842 | 0.0407 |  | H24B | 0.7854 | 0.7309 | 0.0855 |  |
| H26A | 1.0022 | 0.3922 | −0.0081 |  | H26B | 0.5412 | 0.6623 | −0.0149 |  |
| H27A | 1.0343 | 0.4047 | −0.0954 |  | H27B | 0.5592 | 0.6339 | −0.1034 |  |
| H28A | 1.2285 | 0.4648 | −0.1234 |  | H28B | 0.6857 | 0.5418 | −0.1295 |  |
| H29A | 1.4007 | 0.5001 | −0.0683 |  | H29B | 0.8074 | 0.4744 | −0.0664 |  |
| H30A | 1.3799 | 0.4783 | 0.0182 |  | H30B | 0.7950 | 0.5039 | 0.0191 |  |

**Table 5.** Bond distances Å

| | | | |
|---|---|---|---|
| N1A—C5A | 1.366(8) | N1B—C5B | 1.334(7) |
| N1A—C7A | 1.393(7) | N1B—C7B | 1.395(8) |
| N2A—C1A | 1.452(7) | N2B—C1B | 1.440(7) |
| N2A—C3A | 1.340(7) | N2B—C3B | 1.369(7) |
| N2A—C19A | 1.415(7) | N2B—C19B | 1.442(7) |
| O1A—C5A | 1.227(8) | O1B—C5B | 1.225(8) |
| O2A—C3A | 1.234(7) | O2B—C3B | 1.228(7) |
| C1A—C2A | 1.344(8) | C1B—C2B | 1.304(8) |
| C1A—C25A | 1.459(8) | C1B—C25B | 1.488(8) |
| C2A—C5A | 1.508(8) | C2B—C5B | 1.465(8) |
| C3A—C6A | 1.485(8) | C3B—C6B | 1.463(8) |
| C4A—C6A | 1.337(8) | C4B—C6B | 1.318(8) |
| C4A—BR1A | 1.921(7) | C4B—BR1B | 1.874(6) |
| C4A—C13A | 1.452(9) | C4B—C13B | 1.487(8) |
| C7A—C8A | 1.381(9) | C7B—C8B | 1.358(9) |
| C7A—C12A | 1.376(9) | C7B—C12B | 1.366(9) |
| C8A—C9A | 1.351(11) | C8B—C9B | 1.406(8) |
| C9A—C10A | 1.343(11) | C9B—C10B | 1.313(11) |
| C10A—C11A | 1.364(11) | C10B—C11B | 1.393(11) |
| C11A—C12A | 1.398(10) | C11B—C12B | 1.374(11) |
| C13A—C14A | 1.589(10) | C13B—C14B | 1.382(9) |
| C13A—C18A | 1.366(10) | C13B—C18B | 1.378(9) |
| C14A—C15A | 1.355(11) | C14B—C15B | 1.361(10) |
| C15A—C16A | 1.344(12) | C15B—C16B | 1.381(11) |
| C16A—C17A | 1.362(12) | C16B—C17B | 1.332(11) |
| C17A—C18A | 1.367(12) | C17B—C18B | 1.402(12) |
| C19A—C20A | 1.352(10) | C19B—C20B | 1.377(8) |
| C19A—C24A | 1.387(10) | C19B—C24B | 1.370(8) |
| C20A—C21A | 1.401(11) | C20B—C21B | 1.381(8) |
| C21A—C22A | 1.304(14) | C21B—C22B | 1.382(10) |
| C22A—C23A | 1.364(15) | C22B—C23B | 1.351(10) |
| C23A—C24A | 1.360(10) | C23B—C24B | 1.396(8) |
| C25A—C26A | 1.394(9) | C25B—C26B | 1.381(9) |
| C25A—C30A | 1.413(8) | C25B—C30B | 1.381(9) |
| C26A—C27A | 1.360(10) | C26B—C27B | 1.389(10) |
| C27A—C28A | 1.361(11) | C27B—C28B | 1.301(10) |
| C28A—C29A | 1.361(11) | C28B—C29B | 1.411(9) |
| C29A—C30A | 1.333(6) | C29B—C30B | 1.353(10) |

*al.*, 1980) equal to 1.865 Å. Both carbonyl groups are *trans* to phenyl rings, whereas bromine is *cis* with respect to the nearest carbonyl group. Inspection of torsion angles shows that the backbone of the two independent molecules as well as their phenyl rings II and III are in a nearly enantiomorphic relation with the greatest discrepancy for the C1-C2-C5-O1 angle equal to 11.91°. Two other phenyl rings I and IV packed against its counterpart from the other molecule show greater deviation from the mirror symmetry because of packing forces. Molecules A and B are connected by two hydrogen bonds thus forming a dimer. The geometry of the hydrogen bonds is as follows:

$$\mathrm{N1A{-}O2B} = 2.925(7),\ \mathrm{N1A{-}H1A{-}O2B} = 156.18(1.62),$$

$$\mathrm{N1B{-}O2A} = 2.939(6),\ \mathrm{N1B{-}H1B{-}O2A} = 169.85(1.78).$$

Besides, there are two further intermolecular contacts within the dimer:

$$\mathrm{C2A{-}O2B} = 3.173(7),\ \mathrm{C2B{-}O2A} = 3.249(7).$$

**Table 6.** Bond angles/deg[a]

| | Molecule A | | Molecule B | |
|---|---|---|---|---|
| | Angle | esd | Angle | esd |
| C5—N1—C7 | 128.1 | 0.5 | 130.7 | 0.5 |
| C3—N2—C19 | 124.9 | 0.5 | 122.7 | 0.5 |
| C1—N2—C19 | 116.9 | 0.4 | 119.3 | 0.4 |
| C1—N2—C3 | 117.8 | 0.4 | 117.1 | 0.4 |
| N2—C1—C25 | 116.9 | 0.5 | 116.4 | 0.5 |
| N2—C1—C2 | 121.0 | 0.5 | 118.9 | 0.5 |
| C2—C1—C25 | 122.1 | 0.5 | 124.7 | 0.5 |
| C1—C2—C5 | 125.6 | 0.6 | 128.6 | 0.6 |
| N2—C3—O2 | 121.5 | 0.5 | 119.5 | 0.5 |
| O2—C3—C6 | 122.1 | 0.5 | 122.5 | 0.5 |
| N2—C3—C6 | 116.4 | 0.5 | 118.0 | 0.5 |
| BR1—C4—C13 | 115.6 | 0.5 | 117.3 | 0.4 |
| C6—C4—C13 | 125.5 | 0.6 | 124.5 | 0.5 |
| C6—C4—BR1 | 118.9 | 0.5 | 118.2 | 0.5 |
| O1—C5—C2 | 124.0 | 0.6 | 122.8 | 0.6 |
| N1—C5—C2 | 111.9 | 0.6 | 115.5 | 0.5 |
| N1—C5—O1 | 124.0 | 0.5 | 121.7 | 0.5 |
| C3—C6—C4 | 127.4 | 0.6 | 128.0 | 0.5 |
| N1—C7—C12 | 123.3 | 0.6 | 118.1 | 0.5 |
| N1—C7—C8 | 117.0 | 0.5 | 122.9 | 0.5 |
| C4—C13—C18 | 124.5 | 0.6 | 119.8 | 0.6 |
| C4—C13—C14 | 116.6 | 0.6 | 121.0 | 0.6 |
| N2—C19—C24 | 119.7 | 0.6 | 120.3 | 0.5 |
| N2—C19—C20 | 121.3 | 0.6 | 119.9 | 0.5 |
| C1—C25—C30 | 122.7 | 0.5 | 120.9 | 0.5 |
| C1—C25—C26 | 121.1 | 0.5 | 121.3 | 0.5 |

[a] esd following Cruickshank, International Tables, II, 1959, p. 331)

**Table 7.** Torsion angles/deg

| | Molecule A | | Molecule B | |
|---|---|---|---|---|
| | Angle | esd | Angle | esd |
| C5—N1—C7—C8 | 166.9 | 0.6 | 3.3 | 1.0 |
| C7—N1—C5—O1 | 10.2 | 1.0 | −3.7 | 1.0 |
| C7—N1—C5—C2 | −168.0 | 0.6 | 173.8 | 0.6 |
| C3—N2—C19—C24 | 53.3 | 0.8 | 126.3 | 0.6 |
| C1—N2—C19—C24 | −134.6 | 0.6 | −42.4 | 0.7 |
| C1—N2—C3—C6 | −162.9 | 0.5 | 161.7 | 0.5 |
| C19—N2—C3—O2 | −172.7 | 0.5 | 174.3 | 0.5 |
| C1—N2—C3—O2 | 15.1 | 0.8 | −16.7 | 0.8 |
| C3—N2—C1—C25 | −116.6 | 0.6 | 113.8 | 0.6 |
| C3—N2—C1—C2 | 62.3 | 0.7 | −66.4 | 0.7 |
| C19—N2—C1—C25 | 70.7 | 0.6 | −76.9 | 0.6 |
| C19—N2—C1—C2 | −110.5 | 0.6 | 102.9 | 0.6 |
| C19—N2—C3—C6 | 9.2 | 0.8 | −7.3 | 0.8 |
| N2—C1—C25—C30 | −164.5 | 0.5 | −166.7 | 0.5 |
| N2—C1—C2—C5 | 8.8 | 0.9 | 0.3 | 0.9 |
| C2—C1—C25—C26 | −164.8 | 0.6 | −163.8 | 0.6 |
| C25—C1—C2—C5 | −172.5 | 0.6 | −180.0 | 0.6 |
| C1—C2—C5—O1 | 1.9 | 1.0 | −13.8 | 1.0 |
| C1—C2—C5—N1 | −180.0 | 0.6 | 168.7 | 0.6 |
| O2—C3—C6—C4 | 46.9 | 0.9 | −56.6 | 0.9 |
| N2—C3—C6—C4 | −135.0 | 0.7 | 125.1 | 0.6 |
| BR1—C4—C6—C3 | 2.1 | 0.9 | −3.9 | 0.8 |
| C13—C4—C6—C3 | −177.1 | 0.6 | 178.4 | 0.5 |
| BR1—C4—C13—C14 | 163.3 | 0.5 | −161.5 | 0.5 |
| BR1—C4—C13—C18 | −24.7 | 0.9 | 21.7 | 0.8 |

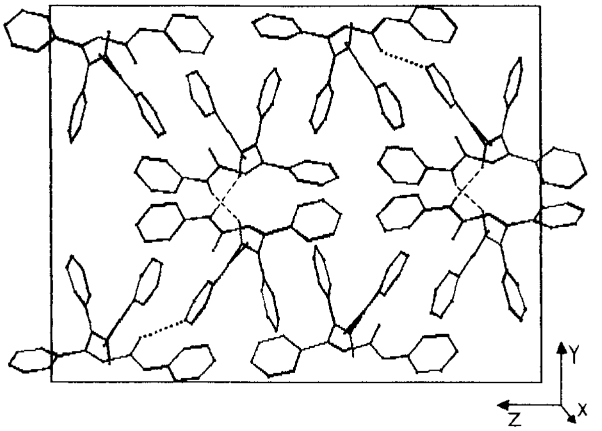

**Fig. 4.** Packing diagram; the dashed line indicates the hydrogen bond and the dotted line the shortest inter-dimer contact.

It is also interesting to note that each molecule has two intramolecular short distances responsible for rigidity of the structure and probably packing as well: O1A—C12A = 2.844(8), N2A—C26A = 2.855(8), O1B—C8B = 2.831(8), N2B—C26B = 2.868(9). The only contact between different dimers detected by us is O1A—C16B = 3.451(9), where O1A belongs to the molecule related by symmetry operation: $-x + 1, y + 1/2, -z + 1/2$, see packing diagram Fig. 4.

X-ray determined molecular structure made the complex spectral image of the investigated molecule clear (see interpretation in spectral section).

Open chain structure of the product of the reaction of benzoylacetanilide with $POBr_3$ gives an evidence that bimolecular condensation takes place instead of cycloaddition. In that respect $POBr_3$ differs considerably from $POCl_3$ in its action towards benzoylacetanilide. The reaction is accompanied by substitution of enolic —OH group by bromine.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60728 (36 pages).