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The Crystal Structure of 1-(α-*o*-Bromobenzoyloxy-*o'*-bromobenzylideneamino)-4,5-diphenyl-1,2,3-triazole

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The crystal structure of 1-(α-*o*-bromobenzoyloxy-*o'*-bromobenzylideneamino)-4,5-diphenyl-1,2,3-triazole, $C_{28}H_{18}N_4O_2Br_2$, has been determined from three-dimensional intensities measured with an automated Philips PW 1100 single-crystal diffractometer (981 independent non-zero reflexions). The structure was determined from the three-dimensional Patterson synthesis by applying the minimum function. The cell constants, obtained by least-squares calculations from direct θ-value measurements on the diffractometer, are: $\alpha = 9{\cdot}4617$ (8), $b = 11{\cdot}1764$ (10), $c = 23{\cdot}4978$ (39) Å, $\beta = 90{\cdot}14$ (1)°, $Z = 4$; the space group is $P2_1/c$. The positional and vibrational parameters, with anisotropic temperature factors for the non-hydrogen atoms, were refined by full-matrix least-squares calculations to a final $R = 0{\cdot}061$. A correction for anomalous scattering by the Br atoms was applied. The molecule has a triazolylisoimide structure. Two of the four benzene rings form, with the central triazole ring, a roughly coplanar system. A characteristic helical chain connects the two benzene rings with the Br atoms to the triazole ring.

Introduction

In the past decade much chemical and spectroscopic work has been done to elucidate the structures of various oxidation products of α-diacylhydrazones. Originally considered as tetrazines, these compounds were eventually shown to be triazole derivatives (Curtin & Alexandrou, 1963; Bauer, Bedford & Katritzky, 1964; Bauer & Katritzky, 1964; Alexandrou, 1966; Alexandrou & Micromastoras, 1968, 1972; Micromastoras, 1969; Petersen & Heitzer, 1970; Bauer, Boulton, Fedeli, Katritzky, Majid-Hamid, Mazza & Vaciago, 1972). Several ambiguities in the results obtained necessitated X-ray crystal structure analysis, which, however, has only been applied so far to 1-(α-benzoyloxybenzylideneamino)-4,5-dimethyl-1,2,3-triazole (Bauer *et al.*, 1972).

The crystal structure determination of 1-(α-*o*-bromobenzoyloxy-*o'*-bromobenzylideneamino)-4,5-diphenyl-1,2,3-triazole (BBDT; $C_{28}H_{18}N_4O_2Br_2$) was undertaken as part of a systematic programme to elucidate the structures of the triazole derivatives prepared at the Laboratory of Organic Chemistry of the Aristotle University of Thessaloniki [see Alexandrou & Micromastoras (1968, 1972) and Micromastoras (1969)].

Experimental

Pure, colourless BBDT crystals were kindly provided by Professor N. E. Alexandrou and Dr E. D. Micromastoras. The crystals are monoclinic, pseudo-orthorhombic plates. A well developed transparent single crystal, with dimensions $0{\cdot}12 \times 0{\cdot}13 \times 0{\cdot}05$ mm, was selected and centred on a computer-controlled Philips PW 1100 four-circle single-crystal diffractometer. With Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71609$ Å) the cell constants were determined first by using the PH (Peak Hunting) routine of the instrument. To achieve greater accuracy, the θ angles of 179 strong reflexions with large θ values were directly measured on the diffractometer and subsequently processed with the least-squares program *PARAM* [part of the X-RAY System of Crystallographic Programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972)]. The final values obtained are given in Table 1. Systematic absences led to the space group $P2_1/c$. The density of the crystals was measured by flotation in potassium bromide solution.

Table 1. *Crystal data for BBDT*

(Standard errors, given in parentheses, refer to last digit).

$C_{28}H_{18}N_4O_2Br_2$	F.W. 601·8
Monoclinic	$Z = 4$
Space group $P2_1/c$	$F(000) = 1200$
$a = 9{\cdot}4617$ (8) Å	$\varrho_{calc} = 1{\cdot}610$ g cm^{-3}
$b = 11{\cdot}1764$ (10)	$\varrho_{meas} = 1{\cdot}603$ g cm^{-3}
$c = 23{\cdot}4978$ (38)	M.p. 130 – 131°C
$\beta = 90{\cdot}14$ (1)°	$\mu = 35{\cdot}20$ cm^{-1}
$V = 2484{\cdot}84$ Å^3	λ(Mo $K\alpha$) = 0·71609 Å

Three-dimensional intensity data were collected with a scintillation counter on the PW 1100 diffractometer in the ω-scan mode, using Mo $K\alpha$ radiation, monochromatized with a graphite monochromator. The intensities of 3731 independent reflexions up to $2\theta = 50°$ (max. $h,k,l = 9, 10, \pm 20$ respectively) were examined and 981 of them with top intensities, I_{top}, given by $I_{top} - 2\sqrt{I_{top}} > I_{bck}$, where I_{bck} is the intensity of the background, were considered as observed and included in all subsequent computations. The remaining 2750 re-

flexions were treated as weak and the Hamilton (1955) correction was applied to them.

Integrated intensities were converted to F_o values in the usual way, by a modified version of the special measurement treatment program by Hornstra & Stubbe (1972). No absorption correction was applied. For all subsequent computations, the programs of the X-RAY System were used throughout.

Determination of the structure and refinement

The structure was essentially solved from the three-dimensional Patterson synthesis by applying the minimum function, but the positions of some C atoms were found from difference Fourier maps. On the Harker line three maxima appeared which could be considered as potential reflexion satellites and the corresponding Patterson sections were compared with the Harker section at $y=\frac{1}{2}$ in the usual way. The positions of the two Br atoms in the asymmetric unit of the cell were immediately clear on the first M_2 map, corresponding to the one Br atom. The M_2 function of the second Br atom was drawn and then combined with the first M_2 to give an M_4 function. Besides the Br atoms the positions of the N, O and some C atoms were revealed. The rest of the C atoms were located from difference Fourier syntheses. A structure-factor calculation at this stage gave $R=0{\cdot}304$.

Refinement of the structure was carried out by full-matrix least-squares calculations, with the program *CRYLSQ* of the X-RAY System. The atomic scattering factors for Br, N, O and C were from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections for Br were taken from *International Tables for X-ray Crystallography* (1968). A single scale factor was used for the whole set of reflexion data.

With isotropic temperature factors and unit weights, refinement reduced R to 0·098 in six cycles. Five further cycles with anisotropic temperature coefficients gave an R of 0·068. The H atoms were then located on a difference synthesis and included in further refinement cycles with isotropic temperature factors assigned to them, equal to those of the C atoms to which they are

Table 2. *Atomic coordinates, anisotropic temperature coefficients* ($\times 10^4$) *and equivalent isotropic temperature factors for the non-hydrogen atoms in BBDT, with standard deviations in parentheses*

Anisotropic temperature factor $T=\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\}$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Br(1)	0·2134 (4)	0·0471 (3)	0·5253 (2)	188 (5)	92 (3)	44 (1)	−16 (4)	21 (2)	18 (2)	7·03
Br(2)	0·3134 (3)	0·1193 (3)	0·0076 (1)	148 (4)	99 (3)	18 (1)	−7 (3)	−3 (1)	11 (1)	4·73
O(1)	0·0380 (17)	0·2082 (15)	0·9474 (6)	113 (24)	76 (18)	12 (4)	4 (18)	10 (7)	−1 (7)	3·52
O(2)	0·9223 (19)	0·1497 (18)	0·4006 (8)	150 (29)	121 (27)	21 (5)	8 (21)	5 (10)	1 (9)	5·39
N(1)	0·9206 (20)	0·1074 (16)	0·8500 (8)	109 (29)	35 (18)	16 (5)	10 (21)	21 (10)	9 (9)	3·02
N(2)	0·8536 (23)	0·0542 (18)	0·8926 (8)	100 (34)	90 (23)	16 (5)	−40 (24)	0 (10)	5 (9)	3·85
N(3)	0·7208 (20)	0·0335 (19)	0·8760 (9)	57 (28)	108 (25)	21 (5)	39 (23)	16 (9)	7 (9)	4·03
N(4)	0·0627 (18)	0·1293 (17)	0·8528 (8)	54 (29)	86 (24)	16 (5)	−36 (23)	−11 (9)	−19 (9)	3·23
C(1)	0·7116 (22)	0·0643 (19)	0·8188 (9)	77 (42)	63 (27)	9 (6)	−57 (27)	14 (13)	0 (10)	2·65
C(2)	0·8362 (25)	0·1109 (22)	0·8021 (9)	99 (34)	71 (24)	14 (6)	−40 (27)	−26 (12)	2 (12)	3·38
C(3)	0·1124 (21)	0·1801 (20)	0·8968 (10)	39 (28)	67 (24)	10 (5)	−8 (22)	−1 (10)	−5 (9)	2·30
C(4)	0·9385 (31)	0·2028 (27)	0·4428 (13)	146 (48)	83 (35)	18 (8)	13 (34)	33 (17)	3 (13)	4·48
C(5)	0·8454 (24)	0·2045 (25)	0·4922 (11)	78 (38)	77 (30)	22 (8)	69 (26)	−5 (14)	2 (12)	3·85
C(6)	0·8320 (27)	0·1913 (36)	0·0214 (10)	113 (42)	274 (58)	1 (6)	−82 (39)	−9 (12)	4 (13)	5·99
C(7)	0·7313 (36)	0·1779 (26)	0·0673 (14)	230 (59)	40 (31)	33 (10)	−28 (35)	−17 (19)	−1 (13)	5·86
C(8)	0·6669 (35)	0·2229 (36)	0·5843 (14)	198 (61)	133 (46)	30 (10)	80 (45)	−20 (18)	−12 (20)	6·77
C(9)	0·6710 (27)	0·1133 (34)	0·5592 (12)	105 (41)	198 (47)	20 (7)	50 (41)	36 (13)	27 (17)	6·03
C(10)	0·7629 (27)	0·1060 (23)	0·5115 (11)	142 (46)	61 (29)	24 (7)	−5 (32)	−15 (14)	37 (13)	4·47
C(11)	0·2586 (22)	0·2220 (22)	0·8965 (10)	29 (34)	107 (33)	14 (6)	36 (27)	7 (12)	−18 (12)	3·14
C(12)	0·3092 (28)	0·2792 (24)	0·8469 (11)	109 (37)	109 (31)	17 (6)	−23 (28)	25 (12)	−8 (11)	4·35
C(13)	0·4426 (35)	0·1775 (24)	0·3429 (11)	209 (56)	100 (31)	10 (6)	36 (33)	36 (15)	−12 (11)	4·89
C(14)	0·5344 (29)	0·1909 (28)	0·3895 (14)	144 (43)	132 (36)	18 (7)	38 (32)	4 (14)	19 (13)	5·28
C(15)	0·4957 (22)	0·2451 (21)	0·9366 (9)	60 (31)	69 (27)	11 (6)	−20 (25)	1 (10)	2 (9)	2·67
C(16)	0·3584 (23)	0·2072 (18)	0·9377 (9)	29 (31)	41 (25)	11 (5)	18 (22)	17 (10)	12 (10)	1·85
C(17)	0·5740 (21)	0·0514 (19)	0·7891 (8)	94 (38)	45 (23)	3 (6)	22 (26)	5 (11)	−5 (10)	2·08
C(18)	0·5264 (25)	0·0286 (21)	0·1901 (10)	127 (43)	73 (33)	22 (8)	−70 (32)	28 (15)	3 (12)	4·38
C(19)	0·6597 (23)	0·0281 (22)	0·2168 (13)	73 (40)	64 (31)	34 (9)	−63 (29)	19 (15)	−24 (14)	4·47
C(20)	0·3121 (29)	0·0415 (32)	0·7336 (12)	130 (44)	153 (38)	17 (7)	50 (36)	−4 (13)	−5 (14)	5·35
C(21)	0·4188 (32)	0·1159 (30)	0·7155 (10)	161 (48)	180 (39)	10 (6)	−36 (40)	−3 (13)	−14 (14)	5·62
C(22)	0·5481 (22)	0·1221 (24)	0·7442 (9)	78 (37)	127 (33)	7 (5)	−14 (35)	−22 (12)	11 (13)	3·60
C(23)	0·8993 (24)	0·1550 (21)	0·7490 (10)	82 (36)	37 (27)	16 (7)	5 (23)	−2 (11)	6 (11)	2·75
C(24)	0·8982 (24)	0·0855 (21)	0·7020 (12)	118 (38)	65 (30)	18 (7)	−16 (24)	15 (13)	−5 (12)	3·82
C(25)	0·9654 (28)	0·1215 (28)	0·6525 (9)	173 (43)	102 (32)	6 (6)	25 (36)	12 (12)	−15 (12)	4·19
C(26)	0·0343 (31)	0·2343 (34)	0·6539 (13)	146 (49)	140 (49)	22 (9)	15 (39)	−21 (16)	22 (15)	5·69
C(27)	0·0363 (30)	0·1992 (27)	0·2005 (16)	132 (48)	88 (34)	41 (11)	84 (33)	−38 (19)	−28 (18)	6·09
C(28)	0·9664 (25)	0·2385 (28)	0·2491 (10)	114 (41)	143 (41)	7 (6)	60 (33)	2 (11)	−7 (12)	4·24

bonded. At this stage the weighting function $w=1/(A+B|F_o|+C|F_o|^2)$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) was introduced and a systematic weight analysis was carried out by employing the programs *WTANAL* and *WTLSSQ* of the X-RAY System. This led to essentially unit weights and consequently the original weighting scheme was kept. Convergence was reached at $R=0{\cdot}061$.

The final positional parameters and anisotropic temperature coefficients for the non-hydrogen atoms are given in Table 2. The final coordinates and isotropic temperature factors for the hydrogen atoms are shown in Table 3. The $|F_o|$ and $|F_c|$ values, obtained from the parameters in Tables 2 and 3, are in Table 4 (for brevity, the unobserved reflexions are omitted). Interatomic distances and bond angles are given in Tables 5 and 6.

Table 3. *Atomic coordinates and isotropic temperature factors for the hydrogen atoms in BBDT*

	x	*y*	*z*	*B*
H(C6)	0·875 (23)	0·178 (19)	0·062 (9)	5·99 Å²
H(C7)	0·740 (22)	0·108 (20)	0·094 (8)	5·86
H(C8)	0·574 (23)	0·253 (20)	0·111 (9)	6·77
H(C9)	0·611 (22)	0·033 (20)	0·555 (9)	6·03
H(C12)	0·209 (20)	0·202 (18)	0·331 (8)	4·35
H(C13)	0·492 (20)	0·108 (18)	0·318 (8)	4·89
H(C14)	0·646 (20)	0·161 (17)	0·388 (8)	5·28
H(C15)	0·584 (17)	0·228 (16)	0·966 (7)	2·67
H(C18)	0·500 (19)	0·047 (18)	0·144 (8)	4·38
H(C19)	0·739 (19)	0·091 (17)	0·207 (8)	4·47
H(C20)	0·203 (20)	0·040 (19)	0·723 (8)	5·35
H(C21)	0·412 (20)	0·112 (19)	0·669 (8)	5·62
H(C22)	0·634 (18)	0·118 (17)	0·713 (7)	3·60
H(C24)	0·842 (19)	0·005 (17)	0·705 (7)	3·82
H(C25)	0·974 (19)	0·071 (17)	0·615 (7)	4·19
H(C26)	0·050 (20)	0·254 (19)	0·108 (8)	5·69
H(C27)	0·083 (21)	0·114 (20)	0·187 (8)	6·09
H(C28)	0·971 (19)	0·188 (17)	0·291 (7)	4·24

Description of the structure and discussion

The structural and conformational features of the BBDT molecule are shown in the clinographic projection of Fig. 1. The compound clearly has a triazolyl-isoimide structure. A characteristic feature is the helical main chain N(4)–C(3)–O(1)–C(4), connecting two benzene rings to the central triazole ring. The helical chain, to which belong also N(1) and N(2), is more clearly seen in the clinographic projection of Fig. 2 (view along the *a* axis).

The triazole and the four benzene rings of the molecule are planar to a good approximation. In Table 7 are listed the various least-squares planes of the BBDT molecule, together with the dihedral angles between them. The two benzene rings *B*2 and *B*3, attached to C(3) and C(1), Fig. 1, form with the triazole ring, *T*, a roughly coplanar system, the angles $B2 \wedge T$ and $B2 \wedge B3$ being 7·3° and 14·5° respectively. The other two benzene rings *B*1 and *B*4 form much larger angles with the other planes (over 65° and 54·5° respectively). In the main chain two planes, *P*1 and *P*2, are distinguished: the first formed by the atoms N(1)–N(4)–

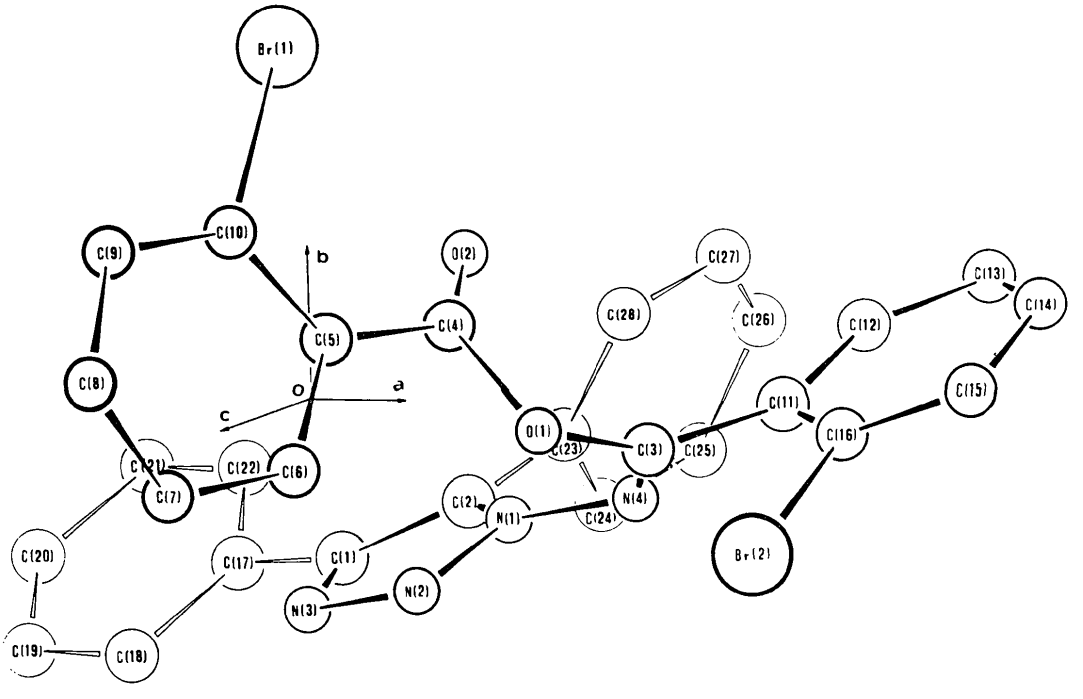

Fig. 1. Clinographic projection of the BBDT molecule showing its conformation.

Table 4. *Observed and calculated structure factors for BBDT*

Table 5. *Interatomic distances* (Å) *in BBDT, with their standard deviations in parentheses*

N(1)—N(2)	1·33 (3)	C(12)–C(13)	1·35 (4)
N(2)—N(3)	1·34 (3)	C(13)–C(14)	1·40 (4)
N(3)—C(1)	1·39 (3)	C(14)–C(15)	1·37 (4)
C(1)—C(2)	1·35 (3)	C(15)–C(16)	1·37 (3)
C(2)—N(1)	1·38 (3)	C(16)–C(11)	1·36 (3)
N(1)—N(4)	1·37 (3)	C(16)–Br(2)	1·96 (2)
N(4)—C(3)	1·27 (3)		
C(3)—O(1)	1·42 (3)	C(1)—C(17)	1·48 (3)
O(1)—C(4)	1·37 (3)	C(17)–C(18)	1·39 (3)
C(4)—O(2)	1·16 (4)	C(18)–C(19)	1·41 (3)
C(4)—C(5)	1·46 (4)	C(19)–C(20)	1·43 (4)
		C(20)–C(21)	1·38 (4)
C(5)—C(6)	1·36 (4)	C(21)–C(22)	1·40 (3)
C(6)—C(7)	1·45 (4)	C(22)–C(17)	1·34 (3)
C(7)—C(8)	1·33 (5)		
C(8)—C(9)	1·36 (5)	C(2)—C(23)	1·47 (3)
C(9)—C(10)	1·42 (4)	C(23)–C(24)	1·35 (4)
C(10)–C(5)	1·42 (4)	C(24)–C(25)	1·39 (4)
C(10)–Br(1)	1·93 (3)	C(25)–C(26)	1·42 (5)
		C(26)–C(27)	1·32 (5)
C(3)—C(11)	1·46 (3)	C(27)–C(28)	1·39 (4)
C(11)–C(12)	1·41 (4)	C(28)–C(23)	1·35 (4)
C(6)—H(C6)	1·1 (2)	C(18)–H(C18)	1·1 (2)
C(7)—H(C7)	1·0 (2)	C(19)–H(C19)	1·0 (2)
C(8)—H(C8)	1·1 (2)	C(20)–H(C20)	1·0 (2)
C(9)—H(C9)	1·1 (2)	C(21)–H(C21)	1·1 (2)
C(12)–H(C12)	1·0 (2)	C(22)–H(C22)	1·1 (2)
C(15)–H(C13)	1·0 (2)		
C(14)–H(C14)	1·1 (2)	C(24)–H(C24)	1·0 (2)
C(15)–H(C15)	1·1 (2)	C(25)–H(C25)	1·0 (2)
		C(26)–H(C26)	1·1 (2)
		C(27)–H(C27)	1·1 (2)
		C(28)–H(C28)	1·1 (2)

Distances of special interest

Br(1)···O(2)	3·09 (2)	O(1)····O(2)	2·22 (2)
Br(2)···O(1)	3·13 (2)	Br(1)···Br(2)	6·949 (5)

C(3)–O(1) and the second by C(3)–O(1)–C(4)–O(2). Plane $P1$ is roughly perpendicular to $B1$ (82·6°) and forms almost equal angles with $B2$ and $B4$(46·2° and 47·9° respectively). Plane $P2$ has a remarkable position: the angles with all the other planes, except $B1$, are almost equal, their values ranging between 62° and 68°. Br(1) and N(4) lie on either side of the plane at a distance ~1 Å.

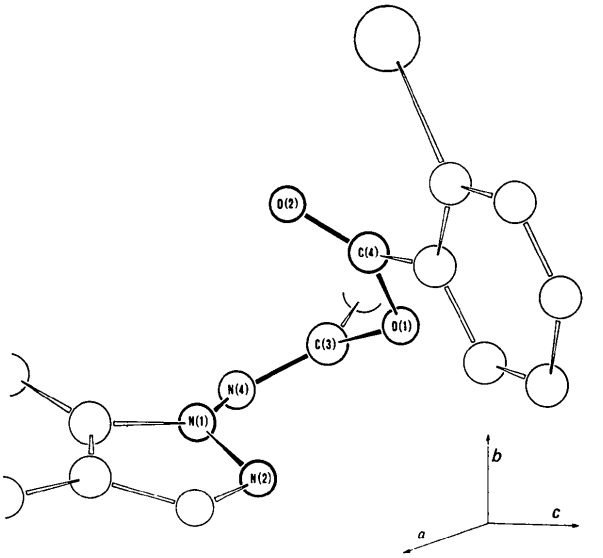

Fig. 2. Clinographic projection of the main-chain helix, viewed along the *a* axis.

Table 6. *Bond angles in BBDT, with their standard deviations in parentheses*

N(1)—N(2)—N(3)	108·0 (1·8)	C(6)—C(7)—C(8)	116·2 (3·0)
N(2)—N(3)—C(1)	107·2 (1·8)	C(7)—C(8)—C(9)	127·5 (3·1)
N(3)—C(1)—C(2)	108·9 (1·9)	C(8)—C(9)—C(10)	114·3 (2·9)
C(1)—C(2)—N(1)	104·8 (1·9)	C(9)—C(10)–C(5)	122·9 (2·6)
C(2)—N(1)—N(2)	110·5 (1·9)	C(10)–C(5)—C(6)	116·8 (2·3)
		C(4)—C(5)—C(6)	118·0 (2·5)
N(2)—N(1)—N(4)	121·1 (1·8)	C(4)—C(5)—C(10)	125·1 (2·5)
C(2)—N(1)—N(4)	126·9 (1·9)	C(5)—C(10)–Br(1)	118·5 (1·8)
N(1)—C(2)—C(23)	117·9 (2·0)	C(9)—C(10)–Br(1)	118·4 (2·1)
C(1)—C(2)—C(23)	137·2 (2·1)		
C(2)—C(1)—C(17)	131·8 (2·0)	C(11)–C(12)–C(13)	122·4 (2·3)
N(3)—C(1)—C(17)	119·0 (1·8)	C(12)–C(13)–C(14)	118·9 (2·5)
		C(13)–C(14)–C(15)	121·4 (2·5)
N(1)—N(4)—C(3)	118·7 (1·8)	C(14)–C(15)–C(16)	115·7 (2·1)
N(4)—C(3)—O(1)	126·8 (1·8)	C(15)–C(16)–C(11)	127·3 (2·0)
N(4)—C(3)—C(11)	119·2 (2·0)	C(16)–C(11)–C(12)	113·9 (2·0)
C(11)–C(3)—O(1)	113·9 (1·9)	C(3)—C(11)–C(12)	118·1 (2·0)
C(3)—O(1)—C(4)	115·8 (1·8)	C(3)—C(11)–C(16)	127·8 (2·1)
O(1)—C(4)—O(2)	121·7 (2·6)	C(11)–C(16)–Br(2)	120·4 (1·7)
O(1)—C(4)—C(5)	110·0 (2·3)	C(15)–C(16)–Br(2)	112·3 (1·6)
C(5)—C(4)—O(2)	127·2 (2·7)	C(17)–C(18)–C(19)	116·9 (2·1)
C(5)—C(6)—C(7)	121·8 (2·9)	C(18)–C(19)–C(20)	122·1 (2·3)
C(19)–C(20)–C(21)	116·5 (2·4)	C(23)–C(24)–C(25)	121·1 (2·3)
C(20)–C(21)–C(22)	121·6 (2·5)	C(24)–C(25)–C(26)	116·8 (2·4)
C(21)–C(22)–C(17)	120·6 (2·3)	C(25)–C(26)–C(27)	121·5 (2·8)
C(22)–C(17)–C(18)	122·0 (1·9)	C(26)–C(27)–C(28)	119·7 (2·9)
C(1)—C(17)–C(18)	119·7 (1·8)	C(27)–C(28)–C(23)	120·1 (2·5)
C(1)—C(17)–C(22)	118·2 (1·9)	C(28)–C(23)–C(24)	120·8 (2·2)
		C(2)—C(23)–C(24)	120·0 (2·1)
		C(2)—C(23)–C(28)	119·1 (2·1)

Part of the structure shows a similarity to that of 1-(α-benzoyloxybenzylideneamino)-4,5-dimethyl-1,2,3-triazole (Bauer *et al.*, 1972), in which the triazole ring is analogously connected to two benzene rings *via* a helical main chain. An essential difference between the two structures, however, is that the corresponding helical main chains, and consequently the two benzene rings *B*1 and *B*2, lie on opposite sides of the triazole-ring plane. The difference may be attributed to the presence of two additional benzene rings and two Br atoms in the BBDT molecule. The angles between ring planes in the two compounds differ considerably. In BBDT they are $B1 \wedge T = 79{\cdot}8°$, $B2 \wedge T = 7{\cdot}3°$ and $B1 \wedge B2 = 75{\cdot}6°$, whereas in the other compound they are 65·5°, 18·5° and 58·4° respectively.

The two Br–C_{ar} bond lengths, 1·93 and 1·96 Å respectively, are longer than the average distance of 1·85 Å given by Sutton (1965). A detailed survey of recent literature, however, showed that this seems to be the rule. The geometrical features of the triazole and the benzene rings are in good agreement with the usually accepted values. Mean bond lengths in the four benzene rings *B*1, *B*2, *B*3 and *B*4 are 1·39, 1·38, 1·38 and 1·37 Å respectively. The four C(sp)^2–C(sp)^2 lengths between the benzene rings and the main chain or the triazole ring, *i.e.* C(1)–C(17) 1·48, C(2)–C(23) 1·47, C(3)–C(11) 1·47 and C(4)–C(5) 1·46 Å, are in good agreement with the value 1·47–1·48 Å suggested by Lide (1962) for a C(sp)^2–C(sp)^2 bond length. The shortening influence of adjacent double bonds is evident in all cases. It is interesting, however, that the corresponding distances in 1-(α-benzoyloxybenzylideneamino)-4,5-dimethyl-1,2,3-triazole (Bauer *et al.*, 1972), are 1·50 or 1·51 Å. The presence of the two Br atoms and the other aromatic rings does not seem to have an important influence on the coplanarity of the systems –N=C–Ar and O=C–Ar. Conjugation between these groups, however, results in shortened C(3)–C(11) and C(4)–C(5) bond lengths.

The intramolecular contact distances Br(1)–O(2) 3·08 and Br(2)–O(1) 3·12 Å are understandably a little shorter than the sum of the van der Waals radii of the corresponding atoms. Other contact distances are within the expected values, with the exception of C(6)–O(1), 2·62 Å, which is very short.

Fig. 3 shows in projection along [010] the molecular packing of BBDT in the unit-cell. The various intermolecular distances are normal. The shortest Br–Br intermolecular distance is 3·87 Å, equal to twice the van der Waals radius.

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Table 7. *Least-squares planes in BBDT, with displacements of atoms from the planes* (Å)

The equation for a plane is in the form $AX+BY+CZ=D$ and refers to orthogonal axes. The coordinates X, Y, Z are expressed in Å; D is the distance of the plane from the origin. Asterisks indicate atoms not included in the calculation of the plane. The mean estimated standard deviations of the atoms defining a plane are given in parentheses attached to the distance of the first atom.

(T) Triazole ring

$$-3{\cdot}0767X+0{\cdot}90918Y+0{\cdot}28058Z=4{\cdot}00382$$

Main chain	N(4)*	−0·145	N(1)	0·028 (27)
	C(3)*	0·516	N(2)	−0·034
	O(1)*	1·352	N(3)	0·027
	C(4)*	2·515	C(1)	−0·010
	O(2)*	2·824	C(2)	−0·010
	Br(2)*	0·046	C(17)*	0·064
			C(23)*	−0·097

(B1) Benzene ring 1 [attached to C(4)]

$$0{\cdot}74216X+0{\cdot}25526Y+0{\cdot}61971Z=21{\cdot}18851$$

C(5)	0·000 (29)	C(4)*	−0·060
C(6)	0·031	Br(1)*	0·048
C(7)	−0·045		
C(8)	0·029	O(1)*	0·450
C(9)	0·004	O(2)*	−0·634
C(10)	−0·019		

(B2) Benzene ring 2 [attached to C(3)]

$$-0{\cdot}29656X+0{\cdot}86726Y+0{\cdot}39990Z=7{\cdot}02657$$

C(11)	0·028 (28)	C(3)*	0·039
C(12)	−0·020	Br(2)*	−0·070
C(13)	−0·013		
C(14)	0·040	N(4)*	−0·725
C(15)	−0·031	O(1)*	0·996
C(16)	−0·003		

(B3) Benzene ring 3 [attached to C(1)]

$$-0{\cdot}34387X+0{\cdot}72222Y+0{\cdot}60013Z=9{\cdot}69125$$

C(17)	−0·002 (24)	C(21)	−0·012
C(18)	−0·026	C(22)	0·021
C(19)	0·035	C(1)*	0·074
C(20)	−0·016		

(B4) Benzene ring 4 [attached to C(2)]

$$0{\cdot}83978X-0{\cdot}44875Y+0{\cdot}30560Z=11{\cdot}71336$$

C(23)	−0·001 (7)	C(28)	−0·005
C(24)	0·002	C(2)*	0·100
C(25)	0·004	N(3)*	0·094
C(26)	−0·010	O(2)*	0·285
C(27)	0·011		

(P1) Plane 1 of the main chain

$$-0{\cdot}17499X+0{\cdot}91094Y-0{\cdot}37359Z=-7{\cdot}89586$$

N(1)	0·011 (23)	C(8)*	0·110
N(4)	−0·025	C(11)*	0·205
C(3)	0·025	C(19)*	0·182
O(1)	−0·012	O(2)*	2·036
C(1)*	0·193		

(P2) Plane 2 of the main chain

$$0{\cdot}70390X+0{\cdot}66040Y+0{\cdot}26152Z=14{\cdot}21855$$

C(3)	−0·007 (15)	C(10)*	0·053
O(1)	0·015	Br(1)*	1·010
C(4)	−0·017	Br(2)*	1·561
O(2)	0·009	N(4)*	−0·981

Table 7 (*cont.*)

Dihedral angles between planes (°)

$T \wedge B1$	79·8	$B1 \wedge B2$	75·6	$B2 \wedge B3$	14·5	$B3 \wedge B4$	64·6	$B4 \wedge P1$	47·9	$P1 \wedge P2$	67·6
$T \wedge B2$	7·3	$B1 \wedge B3$	72·5	$B2 \wedge B4$	58·9	$B3 \wedge P1$	60·4	$B4 \wedge P2$	68·0		
$T \wedge B3$	21·4	$B1 \wedge B4$	45·7	$B2 \wedge P1$	46·2	$B3 \wedge P2$	66·9				
$T \wedge B4$	54·5	$B1 \wedge P1$	82·6	$B2 \wedge P2$	62·1						
$T \wedge P1$	39·0	$B1 \wedge P2$	31·5								
$T \wedge P2$	62·8										

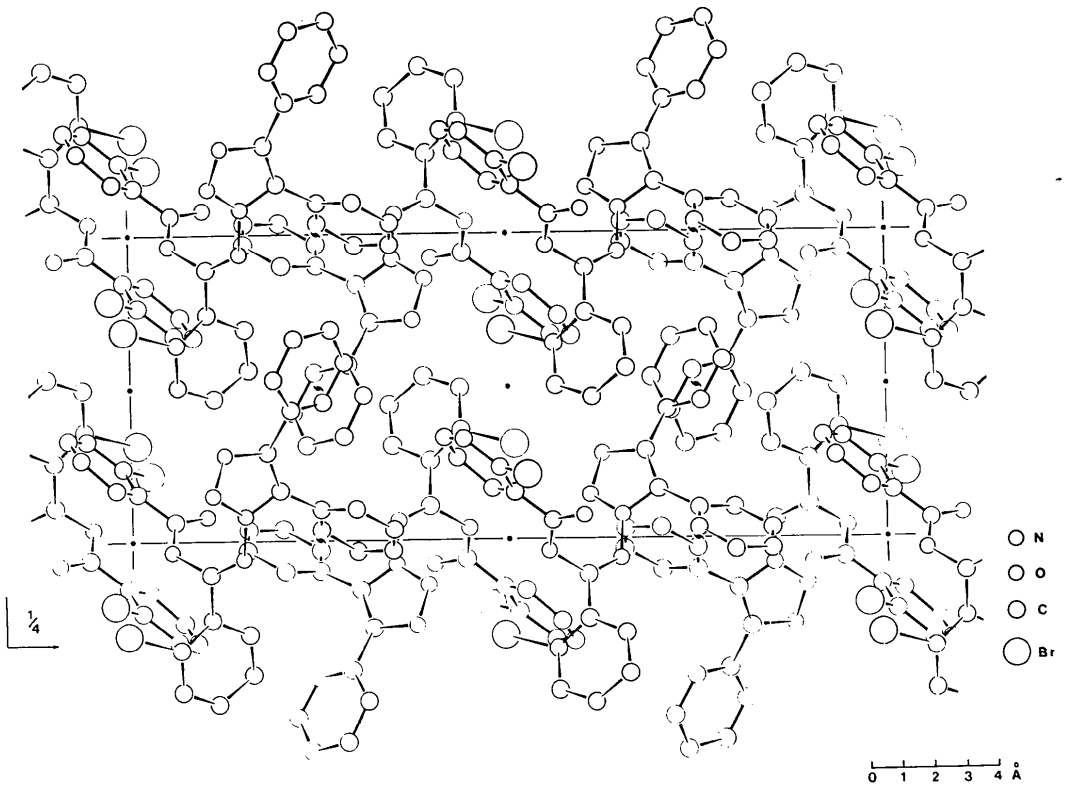

Fig. 3. Projection of the structure of BBDT parallel to **b**.

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