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Bisphenylazostilbene

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Abstract. Monoclinic, $P2_1/c$, $a=11\cdot799$ (4), $b=17\cdot687$ (9), $c=11\cdot046$ (4) Å, $\beta=112\cdot77$ (2)°, $C_{26}H_{20}N_4$, $Z=4$, $D_x=1\cdot22$ g cm^{-3}. This compound, prepared by the iodine oxidation of *anti* benzil osazone, is an essentially planar conjugated system except for the two phenyl groups of the stilbene moiety which are both rotated 57° from the plane of the rest of the molecule. These phenyl groups are in a *trans* relationship about the carbon–carbon double bond.

Introduction. Crystals of the compound, recrystallized from ethanol, were provided by Wintner & Bahn (1971). A $0\cdot2\times0\cdot35\times0\cdot45$ mm crystal was used. Zero and first-level Weissenberg photographs taken with the crystal rotating about the b axis showed systematic absences in $h0l$ for l odd. Precession photographs of $hk0$, hkl, and $0kl$ planes showed systematic absences in $0k0$ reflections for k odd, and determine the space group uniquely as $P2_1/c$. Intensity data were collected on a Picker–Nuclear FACS-I automated diffractometer using the moving-crystal, moving-counter technique, $\theta=2\theta$ scan, with Cu $K\alpha$ radiation, graphite crystal monochromator. All reflections for $5°\le2\theta\le120°$ were measured for the hkl and $hk\bar{l}$ octants of reciprocal space. A total of 3113 unique reflections were measured (not counting space-group extinctions), of which 2881 reflections were considered observed with $F_{\rm obs}$ greater than 2·3 standard deviations (counting statistics). The absorption coefficient μ(Cu $K\alpha$) = 0·67 mm^{-1} gives $\mu R=0\cdot14$, using as R the maximum centre-to-edge distance of the crystal. Standard Lp factors were applied.

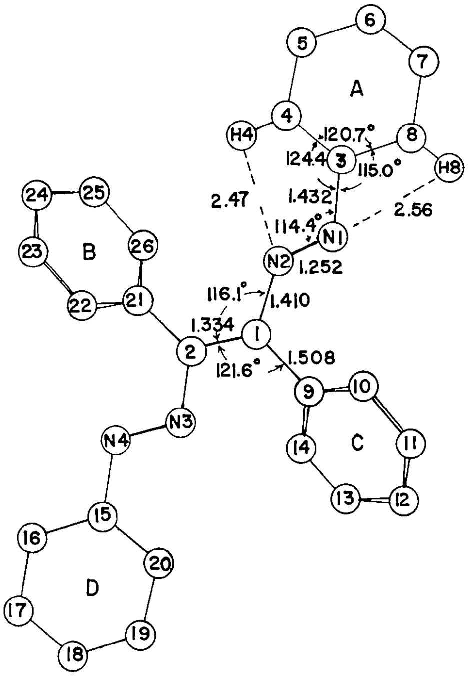

Fig. 1. The bisphenylazostilbene molecule. Bond lengths and angles are averages of the values of symmetry-related pairs.

387 reflections having E values greater than 1·41 were used in centric direct methods programs; the first E map showed clearly 26 of the expected 30 atoms as the largest peaks in the map with probable locations indicated for the other four atoms. A Fourier map using the full data set phased on the locations of the 26 atoms found in the E map showed the remaining four atoms in the expected positions. Block-diagonal least-squares refinement proceeded without difficulty with anisotropic refinement of carbon and nitrogen atom parameters, carried out using 18×18 parameter blocks for atoms taken in pairs. Hydrogen atom positions were calculated after each cycle of refinement assuming all carbon–hydrogen bond lengths to be 1·08 Å and a local bond symmetry of C_{2v} about each carbon–hydrogen bond. These hydrogen coordinates were then used in the structure-factor calculations for the following cycle with the isotropic temperature factor set at 7·0 for all hydrogen atoms. After convergence of refinement, the unweighted residual $R_1=\sum||F_o|-|F_c||/\sum|F_o|=10\cdot9\,\%$, and the weighting scheme, $\omega=[0\cdot200+0\cdot065F_o+0\cdot001F_o^2]^{-1}$, gave uniform values of $\sum\omega(F_o-|F_c|)^2$ in various ranges of F_o. Tables 1 and 2 give the coordinates for all the atoms and the thermal parameters for the carbon and nitrogen atoms. No extraneous peaks were found in a difference Fourier map. The molecular geometry is indicated in Fig. 1 with additional information provided in Tables 3 and 4.*

Discussion. This compound was first prepared by Spasov (Spasov, Elenkov & Robev, 1953) by the iodine oxidation of *anti* benzil osazone. The synthesis was repeated by Woodward & Wintner (1969). With further attention to the details of the reaction. This compound

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* The table and structure factors have been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30108. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final coordinates* (× 10^4)

Estimated standard deviations of the last digit (in parentheses) are given for the atoms refined.

	x	y	z
C(1)	−236 (4)	3871 (2)	805 (4)
C(2)	−1427 (4)	3864 (2)	589 (4)
C(3)	2252 (4)	5053 (2)	2703 (4)
C(4)	1732 (4)	5655 (3)	3066 (5)
C(5)	2458 (6)	6220 (3)	3782 (6)
C(6)	3663 (5)	6217 (3)	4112 (5)
C(7)	4233 (4)	5647 (3)	3787 (5)
C(8)	3521 (5)	5020 (3)	3060 (5)
C(9)	336 (3)	3277 (2)	242 (4)
C(10)	970 (4)	3501 (3)	−530 (4)
C(11)	1522 (4)	2973 (3)	−1022 (5)
C(12)	1475 (5)	2225 (3)	−766 (5)
C(13)	870 (5)	1986 (3)	16 (5)
C(14)	290 (4)	2518 (2)	511 (4)
C(15)	−3995 (4)	2757 (2)	−1407 (4)
C(16)	−5225 (4)	2753 (2)	−1629 (4)
C(17)	−6006 (4)	2242 (3)	−2541 (4)
C(18)	−5509 (4)	1760 (3)	−3171 (4)
C(19)	−4289 (4)	1765 (3)	−2919 (5)
C(20)	−3515 (4)	2253 (3)	−2041 (4)
C(21)	−1951 (4)	4402 (2)	1300 (4)
C(22)	−2960 (4)	4837 (2)	608 (4)
C(23)	−3487 (4)	5307 (3)	1238 (6)
C(24)	−2995 (5)	5338 (3)	2580 (6)
C(25)	−2015 (5)	4901 (3)	3295 (5)
C(26)	−1466 (4)	4430 (3)	2668 (4)
N(1)	1595 (3)	4420 (2)	1953 (4)
N(2)	458 (3)	4466 (2)	1579 (3)
N(3)	−2151 (3)	3310 (2)	−304 (3)
N(4)	−3266 (3)	3300 (2)	−463 (3)
HC(4)	748	5681	2784
HC(5)	2043	6686	4091
HC(6)	4200	6688	4661
HC(7)	5218	5658	4067
HC(8)	3950	4542	2801
HC(10)	1025	4093	−741
HC(11)	2005	3153	−1626
HC(12)	1911	1817	−1174
HC(13)	847	1393	240
HC(14)	−198	2335	1108
HC(16)	−5584	3139	−1108
HC(17)	−6978	2230	−2743
HC(18)	−6101	1366	−3884
HC(19)	−3928	1373	−3429
HC(20)	−2544	2248	−1839
HC(22)	−3348	4810	−451
HC(23)	−4277	5647	680
HC(24)	−3392	5714	3080
HC(25)	−1661	4919	4354
HC(26)	−676	4091	3234

Table 2. *Anisotropic temperature factors* (× 10^4)

The form of the temperature factor is

$$\exp\,[-h^2B_{11}+\ \ldots\ +hkB_{12}+\ \ldots)]\,.$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	95	34	114	−8	61	−2
C(2)	100	39	103	−8	90	3
C(3)	109	34	79	−38	39	−4
C(4)	124	50	142	20	85	−30
C(5)	173	49	190	8	119	−44
C(6)	161	45	145	−39	120	−41
C(7)	104	72	130	−49	98	−34
C(8)	137	55	131	15	120	−28
C(9)	87	38	102	19	57	−8
C(10)	96	47	106	−3	81	−17
C(11)	114	55	133	−10	124	−41
C(12)	144	61	155	20	99	−75
C(13)	142	34	163	−5	7	−20
C(14)	88	42	136	−4	67	−3
C(15)	97	33	87	−31	30	4
C(16)	126	34	129	31	118	−17
C(17)	72	53	133	11	56	13
C(18)	129	40	110	−19	71	−17
C(19)	137	41	136	8	149	−20
C(20)	94	49	133	8	107	10
C(21)	104	31	107	−1	112	−2
C(22)	135	29	133	−6	107	6
C(23)	123	37	197	16	143	9
C(24)	174	46	221	7	270	−28
C(25)	195	56	134	−35	171	−22
C(26)	104	47	125	1	98	12
N(1)	113	40	127	−3	90	−15
N(2)	69	43	119	−8	85	−18
N(3)	67	37	110	−8	80	−17
N(4)	101	40	124	−10	98	−1

Table 3. *Bond lengths* (Å)

C(3)—C(4)	1·364 (7)	C(15)–C(20)	1·384 (7)
C(4)—C(5)	1·354 (7)	C(21)–C(22)	1·375 (5)
C(5)—C(6)	1·322 (9)	C(22)–C(23)	1·377 (8)
C(6)—C(7)	1·336 (8)	C(23)–C(24)	1·368 (9)
C(7)—C(8)	1·435 (7)	C(24)–C(25)	1·361 (7)
C(3)—C(8)	1·394 (7)	C(25)–C(26)	1·393 (8)
C(9)—C(10)	1·392 (7)	C(21)–C(26)	1·394 (6)
C(10)–C(11)	1·367 (7)	C(1)—C(2)	1·332 (6)
C(11)–C(12)	1·357 (8)	C(1)—C(9)	1·506 (6)
C(12)–C(13)	1·383 (9)	C(2)—C(21)	1·510 (6)
C(13)–C(14)	1·393 (8)	C(1)—N(2)	1·402 (5)
C(9)—C(14)	1·381 (6)	C(2)—N(3)	1·418 (5)
C(15)–C(16)	1·374 (6)	C(3)—N(1)	1·430 (5)
C(16)–C(17)	1·401 (6)	C(15)–N(4)	1·434 (5)
C(17)–C(18)	1·369 (7)	N(1)—N(2)	1·245 (5)
C(18)–C(19)	1·356 (7)	N(3)—N(4)	1·258 (5)
C(19)–C(20)	1·354 (6)		

Table 4. *Ring interior angles* (°)

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

has been the subject of a series of studies by Wintner (1970) and Wintner & Bahn (1971) of its thermal and photochemical reactions. Although indirect evidence suggested that the stereochemistry about the central double bond was *trans*, the stereochemistry of the reaction products made it interesting to determine rigorously the geometry. Hence the structure determination reported here was carried out. It is to be noted first of all that *trans* stereochemistry has been unambiguously determined. Rings *A* and *D* and the six connecting atoms form an essentially planar conjugated system. For each benzene ring a plane was determined by least-squares fit to the six carbon atoms of the particular ring. The r.m.s. deviation of all ring atoms from their respective ring planes was 0·007 Å for the set of 24 ring atoms, with a maximum deviation of 0·012 Å.

Tables 3 and 4 show interatomic distances and angles computed with the atom coordinates of Table 1. The least-squares standard deviations for the atom coordinates give standard deviations between 0·004 and 0·009 Å for all the bond lengths and 0·3 to 0·6° for all bond angles. A more realistic estimate of errors is provided by the set of 24 carbon–carbon bond lengths and angles in the four benzene rings. The 24 aromatic ring bond lengths average 1·374 Å with a standard deviation of 0·024 Å. The 24 C–C–C interior angles, Table 4, in the four benzene rings exhibit a standard deviation of 1·3° from the average of 120·0°. As may be seen from Table 3, other pairs of chemically equivalent, bonds, *e.g.* C(15)–N(4) and C(3)–N(1), or N(1)–N(2) and N(3)–N(4), agree to 0·01 Å. Rings *B* and *C* are rotated out of the plane of the conjugated system by an average of 57° about the bonds joining the rings to carbon atoms C(1) and to C(2). This permits normal van der Waals contact distances between the *ortho* hydrogen atoms on rings *B* and *C* and the nearest nitrogen atoms; an average of 2·76 Å was found for these four H···N intramolecular non-bonded distances. Within experimental error the molecular geometry is defined by a twofold molecular rotation axis perpendicular to the plane of the conjugated system and passing midway between C(1) and C(2). Each bond length shown in Fig. 1 is the average of the pair of bonds related by this twofold molecular axis. Each bond angle is likewise the average of a symmetry-related pair. The maximum deviation of any angle shown in Fig. 1 from the average is 1·0°, found for the N(1)–C(3)–C(4) angle. The azo benzene rings appear to be rotated 4° in the plane of the conjugated system; this rotation is probably real and is more likely caused by the intramolecular repulsion of the *ortho* ring hydrogen and the nearest nitrogen atom. Fig. 1 shows the rather short distance of 2·47 Å for this non-bonded atom pair. The average value of 1·25 Å found for the azo N–N bond lengths in this compound is in good agreement with the value of 1·244 Å obtained by Brown (1966*a*) for *p*-azotoluene and the average value of 1·21 Å obtained by Brown (1966*b*) for azobenzene. His C–N bond lengths of 1·433 and 1·452 Å for these two compounds are also within experimental error of the value 1·430 Å reported here for the average phenyl-*N* bond length. Brown's reported C–N–N bond angles of 113·8° (for *p*-azotoluene) and 112·4 (for azobenzene) are also within experimental error of the value of 114·4° reported here.

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1-{1-[3-(*p*-Fluorobenzoyl)propyl]-4-piperidyl}-2-benzimidazolinone (Benperidol)

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Abstract. Rhombohedral (hexagonal setting); $R\bar{3}$; $a=36·6201$ (7), $c=7·7053$ (1) Å; 25°C; $C_{22}H_{24}FN_3O_2$; $M=381·44$; $Z=18$; $F(000)=3636$.

Introduction. Benperidol is a very potent neuroleptic. Transparent hexagonal needles were obtained by very slow evaporation from a 9:1 mixture of *N*,*N*-dimethylformamide and isopropanol.

Experimental. The lattice parameters were obtained by least-squares refinement of the setting angles of 4 reflexions measured with Cu $K\beta$ radiation.

Only reflexions for which $-h+k+l=3n$ (obverse cell) were present on Weissenberg photographs. Hence there are two possibilities for the space group: $R3$ and $R\bar{3}$. The latter was selected on the basis of the distribution of E values ($\langle E^2\rangle=0·9998$; $\langle|E^2-1|\rangle=0·9411$;