

The Crystal and Molecular Structure of 4'-Methylene-1,2-di-*m*-bromophenyl-1',2',6',7'-tetraphenylspiro{pyrazolidine-4,8'-[8'*H*,4'*H*]-benzo[1,2-*c*:4,5-*c'*]dipyrzoline}-3,5,3',5'-tetraone, C₄₇H₃₀N₆O₄Br₂

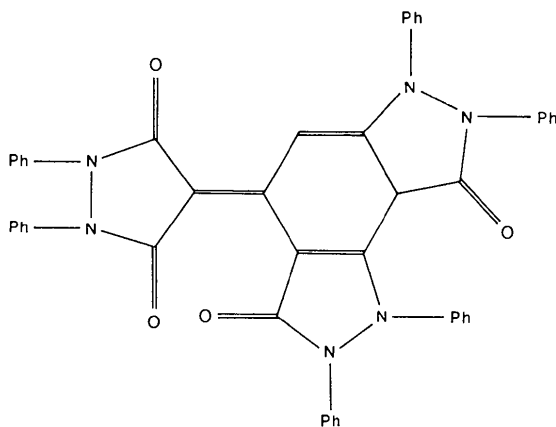
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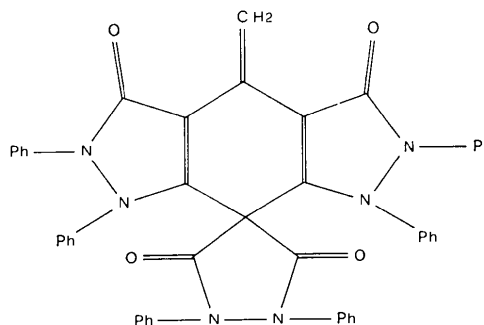
The crystal and molecular structure of the title compound has been determined by single-crystal X-ray diffraction analysis. Crystals are triclinic, space group $P\bar{1}$, with $a=12.775$, $b=12.702$, $c=13.158$ Å, $\alpha=111.33^\circ$, $\beta=97.42^\circ$, $\gamma=88.71^\circ$. The structure was solved by Patterson and Fourier methods, and refined by least-squares methods to a final R value of 0.067 for 2230 observed reflexions.

Introduction

Pyrazolidine and its derivatives are interesting, from a pharmaceutical point of view, as antipyretic agents. In an attempt to obtain new active compounds, recent studies on the chemical behaviour of 1,2-diphenylpyrazolidine-3,5-dione showed that the action of acetic anhydride on this compound (reaction *A*) gives a new complex substance which crystallizes in yellowish tiny irregular tablets with high melting point (323–325°C) (Mangiavacchi, Lazzi & Ridi, 1966). The same compound was also obtained by reaction of 1,2-diphenylpyrazolidine-3,5-dione with 1-(1,2-diphenyl-3,5-diketo-4-pyrazolidine)-1-(1,2-diphenyl-3,5-diketo-4-pyrazolidiniden)ethane (reaction *B*). Further chemical studies to characterize the reaction product (Mangiavacchi, 1968) have assigned it the elementary formula C₄₇H₃₂N₆O₄; the molecular structure proposed on the basis of infrared and n.m.r. spectra as well as chemical evidence, was:



Since some doubts about the molecular structure still remained, the X-ray analysis of a brominated derivative of the compound was undertaken. The structural study showed that the proposed formula is not correct, the right one being:



Experimental

Crystals of the title compound, C₄₇H₃₀N₆O₄Br₂, were prepared and kindly supplied by Dr Mangiavacchi of the Institute of Pharmaceutical Chemistry of Siena University. They are very small pale yellowish needles with rhombic section, melting point 302–304°C.

Preliminary rotation, Weissenberg and precession photographs showed that they are triclinic and gave rough unit-cell constants which were subsequently refined by the least-squares method from fourteen accurate 2θ values measured on a diffractometer. The refined values are: $a=12.775 \pm 0.003$, $b=12.702 \pm 0.001$, $c=13.158 \pm 0.002$ Å, $\alpha=111.33 \pm 0.01^\circ$, $\beta=97.42 \pm 0.02^\circ$, $\gamma=88.71 \pm 0.01^\circ$. * Cell volume is 1971.7 Å³.

The space group $P\bar{1}$ was assumed at the beginning of the present investigation on the basis of morphological evidence. The number of molecules in the unit cell was also assumed to be 2, according to the empirical criterion proposed by Kempster & Lipson (1972). Both assumptions were later confirmed by structural analysis. The calculated density is 1.500 g cm⁻³.

The needle crystals were elongated along $[\bar{1}01]$. The reflexions were collected and indexed according to a

* This cell is not a Delaunay reduced cell. The Delaunay reduction gives a cell with parameters: $a=12.775$, $b=12.702$, $c=14.591$ Å; $\alpha=122.86^\circ$, $\beta=95.86^\circ$, $\gamma=91.29^\circ$. The transformation matrix from our cell to Delaunay cell is $[100/070/011]$.

B -centered cell having $a'=[101]$; $b'=b$; $c'=[\bar{1}01]$. All subsequent calculations were performed with reference to the above primitive cell.

The crystal used for data collection, with dimensions $0.36 \times 0.08 \times 0.08$ mm, was mounted with its longest dimension coincident with the axis of a Hilger and Watts four-circle automatic diffractometer. Intensity data were collected by the ω - 2θ scan technique

with zirconium-filtered Mo radiation. Scans of 60 s with steps of 0.01° and a count of 1 s for each step were taken across the peaks; background was counted for 20 s on each side of the peak. As a check on electronic and crystal stability during data collection three standard reflexions were monitored every 100 measurements. A total of 4750 intensities were measured within the sphere $2\theta \leq 44^\circ$. Beyond this limit only a few re-

Table 1. Fractional atomic coordinates and thermal parameters, with standard deviations

	x/a	y/b	z/c	B (\AA^2)
Br(1)	0.3951(1)	0.5953(1)	1.1159(1)	6.86*
Br(2)	-0.0108(1)	0.1800(1)	1.1069(1)	7.01*
O(1)	0.3643(5)	0.0854(6)	0.2887(6)	3.78(17)
O(2)	0.4492(6)	-0.2523(6)	0.5160(6)	3.82(17)
O(3)	0.0873(6)	0.0127(6)	0.5915(6)	3.96(18)
O(4)	0.3796(6)	0.2560(6)	0.7658(5)	3.42(17)
N(1)	0.2768(7)	0.2152(7)	0.4197(7)	3.07(20)
N(2)	0.2507(6)	0.2285(7)	0.5258(6)	2.77(20)
N(3)	0.3103(6)	-0.0544(7)	0.7077(7)	2.98(20)
N(4)	0.3709(6)	-0.1557(7)	0.6706(7)	3.00(20)
N(5)	0.1195(6)	0.1737(7)	0.7425(7)	2.69(19)
N(6)	0.2121(6)	0.2404(7)	0.8026(6)	2.65(19)
C(1)	0.2597(8)	0.1042(8)	0.6381(8)	2.16(23)
C(2)	0.3162(8)	-0.0040(8)	0.6311(8)	2.48(23)
C(3)	0.3665(7)	-0.0697(8)	0.5466(8)	1.96(22)
C(4)	0.3730(8)	-0.0478(8)	0.4475(8)	2.38(23)
C(5)	0.3257(8)	0.0586(8)	0.4533(8)	2.33(23)
C(6)	0.2783(8)	0.1262(8)	0.5387(8)	2.45(23)
C(7)	0.3269(8)	0.1141(9)	0.3774(9)	3.46(26)
C(8)	0.4011(9)	-0.1685(9)	0.5718(9)	3.32(26)
C(9)	0.1453(9)	0.0894(9)	0.6503(9)	3.04(25)
C(10)	0.2962(9)	0.2072(9)	0.7421(9)	2.95(25)
C(11)	0.4178(8)	-0.1190(9)	0.3633(8)	3.25(25)
C(12)	0.2844(8)	0.3116(9)	0.3917(9)	2.96(25)
C(13)	0.2362(9)	0.3070(10)	0.2917(10)	4.51(29)
C(14)	0.2435(9)	0.4017(12)	0.2619(11)	6.14(35)
C(15)	0.2988(11)	0.4935(11)	0.3359(11)	5.52(33)
C(16)	0.3444(10)	0.5005(10)	0.4338(10)	5.11(32)
C(17)	0.3394(9)	0.4063(10)	0.4654(9)	3.88(28)
C(18)	0.0575(10)	0.2090(10)	0.4868(9)	4.24(29)
C(19)	-0.0419(11)	0.2593(12)	0.4974(11)	6.31(35)
C(20)	-0.0474(12)	0.3709(13)	0.5590(12)	7.02(38)
C(21)	0.0386(12)	0.4353(11)	0.6127(11)	6.13(35)
C(22)	0.1409(9)	0.3878(10)	0.6061(9)	4.44(29)
C(23)	0.1460(8)	0.2760(9)	0.5413(8)	3.01(25)
C(24)	0.2009(8)	0.3554(9)	0.8762(8)	2.64(24)
C(25)	0.1059(9)	0.4105(10)	0.8647(9)	3.54(26)
C(26)	0.1002(10)	0.5220(11)	0.9386(10)	5.02(31)
C(27)	0.1832(10)	0.5723(10)	1.0118(10)	4.73(30)
C(28)	0.2757(9)	0.5193(9)	1.0192(9)	3.82(28)
C(29)	0.2865(8)	0.4053(9)	0.9524(8)	3.02(25)
C(30)	0.0351(9)	0.1606(8)	0.8001(9)	3.06(25)
C(31)	0.0522(8)	0.1796(8)	0.9083(8)	2.78(24)
C(32)	-0.0318(9)	0.1598(9)	0.9573(9)	3.92(28)
C(33)	-0.1295(9)	0.1250(9)	0.8986(10)	4.23(28)
C(34)	-0.1453(9)	0.1114(10)	0.7920(10)	4.49(30)
C(35)	-0.0641(9)	0.1309(9)	0.7386(9)	3.80(27)
C(36)	0.3393(8)	0.0101(8)	0.8244(8)	2.54(24)
C(37)	0.4361(9)	0.0581(9)	0.8657(9)	3.55(27)
C(38)	0.4599(10)	0.1214(10)	0.9778(10)	5.22(32)
C(39)	0.3824(10)	0.1285(10)	1.0447(10)	4.84(30)
C(40)	0.2854(10)	0.0793(10)	1.0043(10)	4.44(29)
C(41)	0.2607(9)	0.0187(9)	0.8925(9)	3.56(26)
C(42)	0.3640(9)	-0.2400(9)	0.7162(8)	2.90(25)
C(43)	0.2720(9)	-0.2566(10)	0.7517(9)	4.03(28)
C(44)	0.2702(10)	-0.3413(11)	0.7956(10)	5.19(32)
C(45)	0.3560(11)	-0.4044(10)	0.8014(10)	5.15(32)
C(46)	0.4475(10)	-0.3897(10)	0.7637(9)	4.54(30)
C(47)	0.4510(9)	-0.3036(10)	0.7217(9)	3.66(27)

Table 1 (cont.)

H(C13)	0.193	0.232	0.236
H(C14)	0.207	0.401	0.183
H(C15)	0.305	0.564	0.313
H(C16)	0.387	0.576	0.488
H(C17)	0.375	0.408	0.544
H(C18)	0.065	0.120	0.437
H(C19)	-0.112	0.209	0.460
H(C20)	-0.125	0.407	0.565
H(C21)	0.029	0.523	0.657
H(C22)	0.212	0.437	0.652
H(C25)	0.040	0.370	0.803
H(C26)	0.028	0.568	0.935
H(C27)	0.176	0.659	1.066
H(C29)	0.358	0.360	0.961
H(C31)	0.128	0.209	0.956
H(C33)	-0.194	0.110	0.938
H(C34)	-0.222	0.084	0.746
H(C35)	-0.077	0.124	0.653
H(C37)	0.496	0.047	0.812
H(C38)	0.535	0.162	1.011
H(C39)	0.399	0.176	1.131
H(C40)	0.227	0.086	1.058
H(C41)	0.184	-0.023	0.859
H(C43)	0.204	-0.206	0.746
H(C44)	0.200	-0.358	0.824
H(C45)	0.354	-0.467	0.836
H(C46)	0.515	-0.444	0.765
H(C47)	0.523	-0.287	0.693
H'(C11)	0.423	-0.106	0.289
H''(C11)	0.453	-0.199	0.357

* B values of Br(1) and Br(2) are the equivalent isotropic temperature factors proposed by Hamilton (1959). The anisotropic temperature factors of Br(1) and Br(2) in the form $T = \exp \{ -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}) \times 10^{-4} \}$ are as follows:

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	168 (2)	71 (1)	76 (1)	-30 (1)	-3 (1)	3 (1)
Br(2)	92 (1)	186 (2)	103 (2)	18 (1)	44 (1)	71 (2)

flexions had intensities above background. Standard deviations on intensities were calculated according to the expression used by Doedens & Ibers (1967): $\sigma(I) = [P + 0.25(B_1 + B_2)(T_p/T_B)^2 + (0.03 I)^2]^{1/2}$ where P is the total peak count in a scan of time T_p , B_1 and B_2 are the background counts each in a time T_B , I is the intensity, equal to $P - 0.5(T_p/T_B)(B_1 + B_2)$; reflexions with $I < 3\sigma(I)$ were considered unobserved and excluded from further computations. The Lorentz-polarization correction was applied. The absorption correction was neglected owing to the small dimensions of the crystal and the low absorption coefficient ($\mu = 22.4 \text{ cm}^{-1}$ for Mo $K\alpha$).

Structure determination and refinement

The coordinates for the two independent Br atoms in the cell were readily deduced from a three-dimensional Patterson function. In this way only about 15% of the electrons in the cell were located (conventional $R \approx 0.56$) and Fourier and difference Fourier syntheses, computed with the signs from bromide atoms, failed to show any groups of maxima which had any chem-

ical significance. An α -synthesis was then computed (Raman, 1961) from which it was possible to find 16 atoms. These atoms were considered to be carbon atoms ($R \approx 0.48$). A Fourier synthesis was computed using as coefficients the structure factors phased from this fragment of the molecule, and with amplitudes multiplied by $w = \tanh(F_{\text{obs}} \cdot F_P / \sum_j f_{Mj}^2)$ where F_P is the

contribution to the amplitude by the partially known structure and f_{Mj} is the scattering factor of the missing j th atom (Woolfson, 1956). This map, which was very well resolved, gave the locations of 25 new atoms ($R = 0.39$). Successive Fourier syntheses revealed the whole structure and improved the model to give an R value of 0.26.

At this stage the refinement of the structure was continued by the least-squares method with the full-matrix program *ORFLS*. The quantity minimized was: $w[|F_o| - |F_c|]^2$, with weights w assigned as $1/[\sigma(F)]^2$. In three cycles, with individual isotropic thermal parameters, R was lowered to 0.13.

Because of the unfavourable observations-to-parameters ratio, the possibility of refining all the atoms anisotropically was ruled out.

Two more cycles performed with anisotropic thermal parameters for the bromine atoms alone, reduced R to 0.08. At this stage the contribution of the hydrogen atoms at theoretical positions computed assuming the value 1.075 Å for the C-H bond length and thermal parameters equal to those of the carbon atoms to which they are bonded was introduced. A final cycle, refining only the non-hydrogen atoms, yielded the coordinates, thermal parameters and relative standard deviations listed in Table 1. The R value reached the final value 0.067 for 2230 observed reflexions. The atomic scattering factors used were those listed for Br, O, N, C and H in *International Tables for X-ray Crystallography* (1962); an anomalous dispersion correction was applied to the bromine scattering curve. Observed and calculated structure factors are given in Table 2.

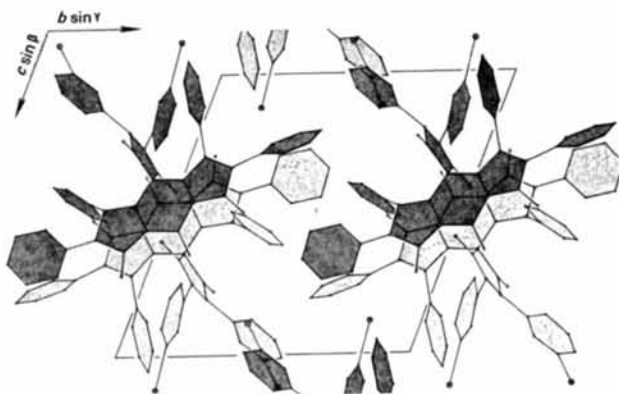


Fig. 1. The cell contents projected along the a axis.

fectly planar, with the two nitrogen atoms in each ring displaced on opposite sides of the ring plane; equations of the best planes and atomic deviations from planarity

are reported in Table 5 (planes *B*, *C* and *D*). Phenyl rings are planar within the limits of experimental error (see Table 5, planes *E* to *J*).

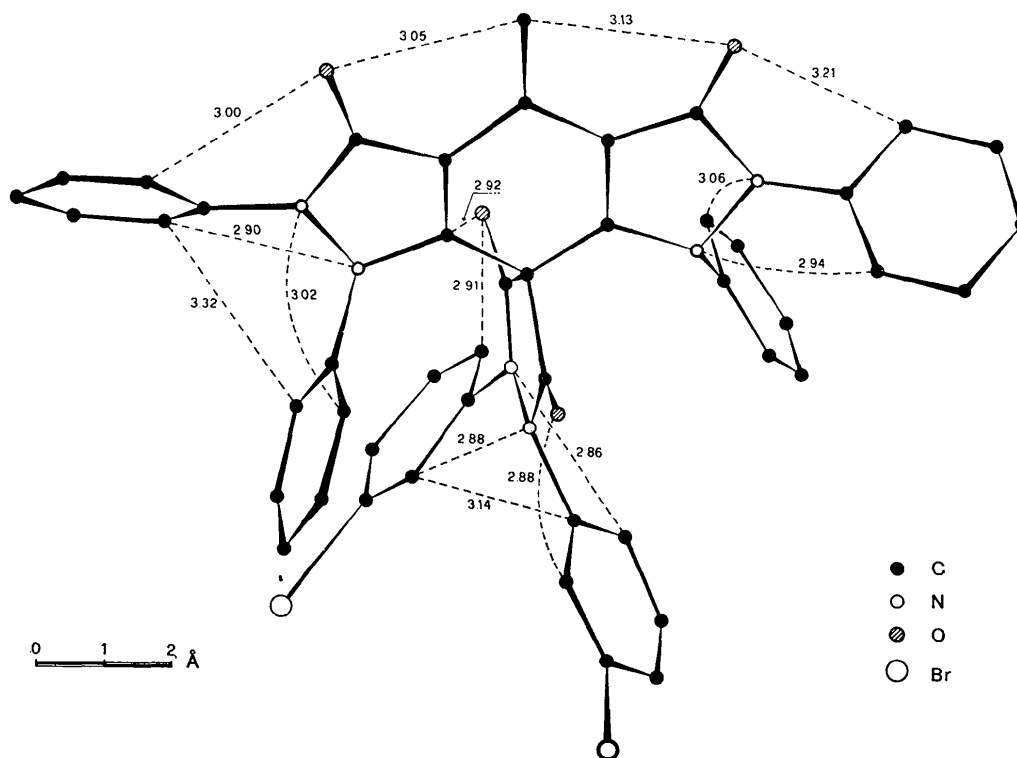


Fig. 2. The molecule as viewed along the *a* axis.



Fig. 3. The molecule as viewed along a direction lying in the plane of the three condensed rings.

Table 3. Bond distances

Estimated standard deviations are between 0.012 and 0.018 Å

Br(1)—C(28)	1.88 Å	C(13)—C(14)	1.40 Å
Br(2)—C(32)	1.87	C(14)—C(15)	1.36
O(1)—C(7)	1.25	C(15)—C(16)	1.32
O(2)—C(8)	1.25	C(16)—C(17)	1.41
O(3)—C(9)	1.20	C(18)—C(19)	1.41
O(4)—C(10)	1.19	C(18)—C(23)	1.38
N(1)—N(2)	1.43	C(19)—C(20)	1.36
N(1)—C(7)	1.38	C(20)—C(21)	1.34
N(1)—C(12)	1.41	C(21)—C(22)	1.43
N(2)—C(6)	1.40	C(22)—C(23)	1.37
N(2)—C(23)	1.46	C(24)—C(25)	1.41
N(3)—N(4)	1.44	C(24)—C(29)	1.37
N(3)—C(2)	1.39	C(25)—C(26)	1.40
N(3)—C(36)	1.46	C(26)—C(27)	1.33
N(4)—C(8)	1.36	C(27)—C(28)	1.36
N(4)—C(42)	1.42	C(28)—C(29)	1.41
N(5)—N(6)	1.43	C(30)—C(31)	1.34
N(5)—C(9)	1.37	C(30)—C(35)	1.37
N(5)—C(30)	1.44	C(31)—C(32)	1.39
N(6)—C(10)	1.39	C(32)—C(33)	1.37
N(6)—C(24)	1.45	C(33)—C(34)	1.34
C(1)—C(2)	1.52	C(34)—C(35)	1.40
C(1)—C(6)	1.48	C(36)—C(37)	1.35
C(1)—C(9)	1.51	C(36)—C(41)	1.41
C(1)—C(10)	1.54	C(37)—C(38)	1.39
C(2)—C(3)	1.35	C(38)—C(39)	1.39
C(3)—C(4)	1.44	C(39)—C(40)	1.35
C(3)—C(8)	1.46	C(40)—C(41)	1.39
C(4)—C(5)	1.45	C(42)—C(43)	1.37
C(4)—C(11)	1.34	C(42)—C(47)	1.37
C(5)—C(6)	1.35	C(43)—C(44)	1.40
C(5)—C(7)	1.42	C(44)—C(45)	1.35
C(12)—C(13)	1.36	C(45)—C(46)	1.37
C(12)—C(17)	1.38	C(46)—C(47)	1.40

Table 4 (cont.)

C(4)—C(3)—C(8)	128.4	C(10)—N(6)—C(24)	122.6
C(3)—C(4)—C(5)	111.2	N(1)—C(12)—C(13)	118.1
C(3)—C(4)—C(11)	122.5	N(1)—C(12)—C(17)	119.5
C(5)—C(4)—C(11)	126.3	C(13)—C(12)—C(17)	122.4
C(4)—C(5)—C(6)	124.3	C(12)—C(13)—C(14)	118.9
C(4)—C(5)—C(7)	127.5	C(13)—C(14)—C(15)	117.3
C(6)—C(5)—C(7)	108.1	C(14)—C(15)—C(16)	124.8
C(1)—C(6)—C(5)	127.5	C(15)—C(16)—C(17)	119.1
C(1)—C(6)—N(2)	121.6	C(16)—C(17)—C(12)	117.4
C(5)—C(6)—N(2)	110.9	N(2)—C(23)—C(18)	119.4
C(5)—C(7)—O(1)	130.9	N(2)—C(23)—C(22)	117.7
C(5)—C(7)—N(1)	106.9	C(18)—C(23)—C(22)	122.9
O(1)—C(7)—N(1)	122.2	C(23)—C(18)—C(19)	118.0
C(3)—C(8)—O(2)	128.9	C(18)—C(19)—C(20)	119.4
C(3)—C(8)—N(4)	107.2	C(19)—C(20)—C(21)	122.4
O(2)—C(8)—N(4)	123.9	C(20)—C(21)—C(22)	120.3
C(1)—C(9)—O(3)	125.4	C(21)—C(22)—C(23)	116.9
C(1)—C(9)—N(5)	109.6	N(3)—C(36)—C(37)	122.2
O(3)—C(9)—N(5)	124.8	N(3)—C(36)—C(41)	116.3
C(1)—C(10)—O(4)	127.3	C(41)—C(36)—C(37)	121.6
C(1)—C(10)—N(5)	108.2	C(36)—C(37)—C(38)	120.4
O(4)—C(10)—N(5)	124.4	C(37)—C(38)—C(39)	117.7
C(7)—N(1)—N(2)	109.2	C(38)—C(39)—C(40)	122.3
C(7)—N(1)—C(12)	127.3	C(39)—C(40)—C(41)	120.1
N(2)—N(1)—C(12)	119.2	C(40)—C(41)—C(36)	117.9
C(6)—N(2)—N(1)	104.6	N(4)—C(42)—C(43)	119.8
C(6)—N(2)—C(23)	122.4	N(4)—C(42)—C(47)	117.8
N(1)—N(2)—C(23)	111.2	C(47)—C(42)—C(43)	122.4
C(42)—C(43)—C(44)	117.1	C(33)—C(34)—C(35)	121.6
C(43)—C(44)—C(45)	120.9	C(34)—C(35)—C(30)	117.0
C(44)—C(45)—C(46)	122.1	N(6)—C(24)—C(25)	119.1
C(45)—C(46)—C(47)	117.5	N(6)—C(24)—C(29)	116.9
C(46)—C(47)—C(42)	120.0	C(29)—C(24)—C(25)	123.9
N(5)—C(30)—C(31)	120.9	C(24)—C(25)—C(26)	116.3
N(5)—C(30)—C(35)	116.6	C(25)—C(26)—C(27)	120.6
C(35)—C(30)—C(31)	122.5	C(26)—C(27)—C(28)	122.4
C(30)—C(31)—C(32)	117.7	C(27)—C(28)—Br(1)	121.7
C(31)—C(32)—Br(2)	119.4	C(27)—C(28)—C(29)	120.9
C(31)—C(32)—C(33)	121.6	Br(1)—C(28)—C(29)	117.4
Br(2)—C(32)—C(33)	119.1	C(28)—C(29)—C(24)	115.8
C(32)—C(33)—C(34)	119.3		

Table 4. Bond angles

Estimated standard deviations are between 0.8 and 1.1°

C(2)—C(1)—C(6)	105.9°	C(2)—N(3)—N(4)	104.9°
C(6)—C(1)—C(10)	110.1	C(2)—N(3)—C(36)	120.2
C(10)—C(1)—C(9)	102.1	N(4)—N(3)—C(36)	111.8
C(9)—C(1)—C(2)	108.5	N(3)—N(4)—C(8)	109.3
C(2)—C(1)—C(10)	114.8	N(3)—N(4)—C(42)	120.1
C(6)—C(1)—C(9)	115.8	C(8)—N(4)—C(42)	127.4
C(1)—C(2)—C(3)	126.1	C(9)—N(5)—N(6)	109.9
C(1)—C(2)—N(3)	121.9	C(9)—N(5)—C(30)	122.2
C(3)—C(2)—N(3)	111.6	N(6)—N(5)—C(30)	120.0
C(2)—C(3)—C(4)	124.7	N(5)—N(6)—C(10)	109.7
C(2)—C(3)—C(8)	106.6	N(5)—N(6)—C(24)	119.4

Table 5. Equations of least-squares planes

Equations are in the form $lx + my + nz = p$, where x , y and z are triclinic fractional atomic coordinates referred to the cell axes.

Plane	Atoms defining the plane	l	m	n	p
<i>A</i>	O(1), O(2), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(11)	10.353	4.679	2.670	4.860
<i>B</i>	N(1), N(2), C(5), C(6), C(7)	10.549	3.277	3.667	5.219
<i>C</i>	N(4), N(3), C(2), C(3), C(8)	10.290	4.465	3.002	5.106
<i>D</i>	N(5), N(6), C(1), C(9), C(10)	-2.176	10.774	-9.769	-5.680
<i>E</i>	C(12), C(13), C(14), C(15), C(16), C(17)	11.397	-2.509	-5.292	0.383
<i>F</i>	C(18), C(19), C(20), C(21), C(22), C(23)	-2.430	-7.302	12.742	4.538
<i>G</i>	C(36), C(37), C(38), C(39), C(40), C(41)	-3.656	11.950	-5.744	-5.860
<i>H</i>	C(42), C(43), C(44), C(45), C(46), C(47)	2.782	4.519	9.031	6.393
<i>I</i>	C(30), C(31), C(32), C(33), C(34), C(35)	-3.336	11.812	-1.138	0.898
<i>J</i>	C(24), C(25), C(26), C(27), C(28), C(29)	-5.691	-7.742	11.685	6.342
<i>K</i>	O(1), O(2), N(1), N(2), N(3), N(4), C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(11)	10.488	4.482	2.643	4.917

The three condensed rings are slightly twisted. The extent of torsional buckling is shown in Fig. 3, where the molecule is projected along a direction lying in the best plane through the rings (plane *K*, Table 5).

Some short intramolecular contacts between atoms not directly bonded are reported in Fig. 2. The packing of the molecules is shown in Fig. 1. Pairs of mole-

Table 5 (cont.)

Deviations of atoms ($\times 10^3 \text{ \AA}$) from the least-squares planes:

	A	B	C	D	E	F	G	H	I	J	K
Br(1)										-161	
Br(2)									4		
O(1)	82	-37									49
O(2)	-12		-61								27
O(3)				-151							
O(4)				131							
N(1)	133	-54			11						60
N(2)	208	103				-116					126
N(3)	-13		-32				11				-36
N(4)	42		28					-9			48
N(5)				37					-90		
N(6)				-34						-29	
C(1)	20	203	-53	4							-40
C(2)	80		24								49
C(3)	66		-6								58
C(4)	-27	201	-138								-37
C(5)	-4	72									-40
C(6)	-159	-106									-220
C(7)	64	-14									18
C(8)	31		-15								46
C(9)				-25							
C(10)				18							
C(11)	-121										-108
C(12)					3						
C(13)					-4						
C(14)					-1						
C(15)					8						
C(16)					-8						
C(17)					3						
C(18)						-1					
C(19)						9					
C(20)						-7					
C(21)						-3					
C(22)						11					
C(23)						-10					
C(24)										2	
C(25)										-17	
C(26)										14	
C(27)										7	
C(28)										-24	
C(29)										18	
C(30)									-29		
C(31)									15		
C(32)									6		
C(33)									-13		
C(34)									-1		
C(35)									21		
C(36)							5				
C(37)							-13				
C(38)							12				
C(39)							-3				
C(40)							-5				
C(41)							4				
C(42)								3			
C(43)								-7			
C(44)								2			
C(45)								8			
C(46)								-13			
C(47)								7			

cules related by the inversion centre at $\frac{1}{2}, 0, \frac{1}{2}$ are located in such a way that the system of the three condensed rings and methylene and keto groups are partially overlapped. The distance between the best planes through two adjacent triple ring systems is 3.30 \AA . Intermolecular distances are normal; those shorter than the sum of the van der Waals radii, assuming for Br, O,

N, and C the values $1.85, 1.50, 1.55, 1.75 \text{ \AA}$ respectively, are listed in Table 6. The contact Br(1)-O(4'), 3.35 \AA long, with the C(28)-Br(1) bond approximately pointing towards O(4) [angle C(28)-Br(1)···O(4') = 166°] is perhaps indicative of some 'charge transfer' interaction between oxygen and halogen (Gaultier, Hauw & Schvoerer, 1971).

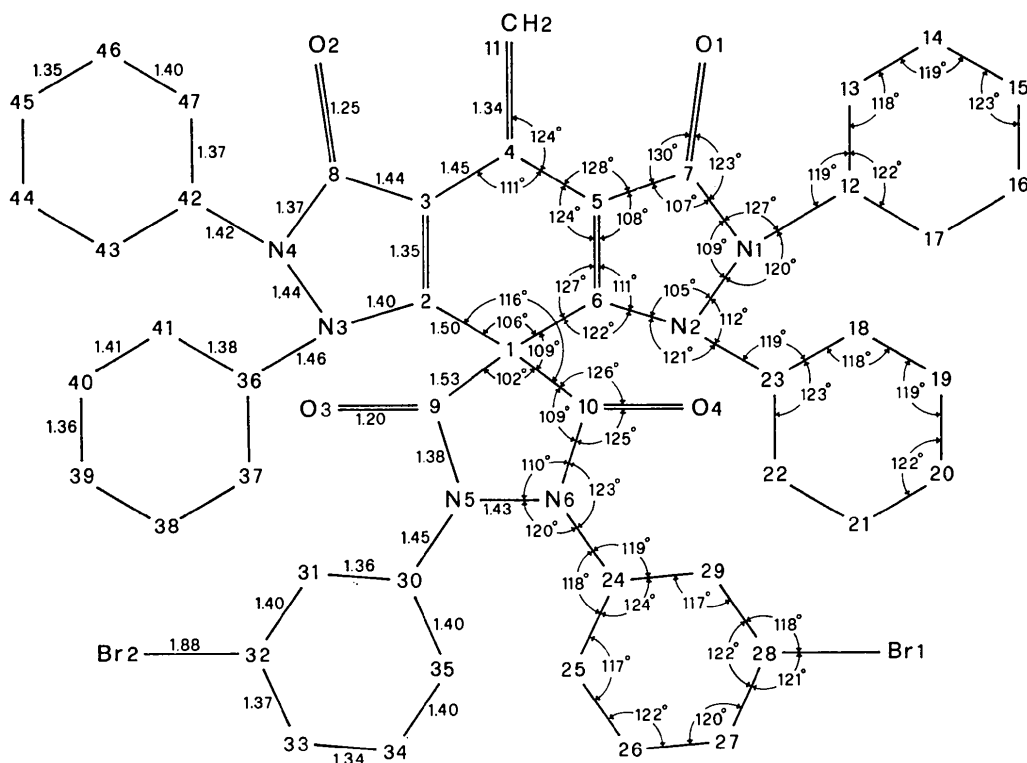


Fig. 4. Molecular dimensions and atomic numbering scheme.

Table 6. Shortest intermolecular approaches

Br(1)—O(4')	(1-x, 1-y, 2-z)	3.35 Å
O(2)—C(16')	(x, -1+y, z)	3.19
O(3)—C(18')	(-x, -y, 1-z)	3.17
C(3)—C(11')	(1-x, -y, 1-z)	3.48
C(4)—C(4')	(1-x, -y, 1-z)	3.42
C(7)—C(8')	(1-x, -y, 1-z)	3.49
C(26)—C(26')	(-x, 1-y, 2-z)	3.36
C(38)—C(38')	(1-x, -y, 2-z)	3.45

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