Larsson, Lundquist, Stålhberg-Stenhagen & Sten-hagen (1969) have made some recent studies of the structural arrangements of lipids in surface layers and interphases. In their studies it was shown that a mono-layer phase can be compressed to a duplex film and successively to a multifilm containing up to 8 layers. Triglycerides in monolayers have the E form while in the solid state they are in the tuning-fork conformation. Compression of triglyceride monolayer beyond the monolayer collapse point produces a duplex layer with molecules of different conformation in the lower and upper parts. They suggest that the upper part is in the tuning-fork arrangement, while the lower part is in the E form.

The interface between the upper and lower parts is hydrophobic. This would suggest that in the case of biological membrane in those regions where the protein interface is hydrophobic the lipid arrangement could be an extended monolayer, while in those regions where the interface is aqueous or ionic the arrangement is the usual bilayer form.

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Crystal and Molecular Structure of 3-p-Bromophenyl-1-nitroso-2-pyrazoline*

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The bromoderivative of the product $C_9H_9N_3O$, obtained when diazomethane is reacted with benzonitrile oxide in ether, has been examined by X-ray single-crystal techniques and shown to have the structure of 3-p-bromophenyl-1-nitroso-2-pyrazoline. The crystals are monoclinic with space group $P2_1/c$ and $a = 5.636 \pm 0.012$, $b = 9.775 \pm 0.021$, $c = 17.516 \pm 0.031$ Å, $\beta = 97.4 \pm 0.2°$. The final R index with all the non-hydrogen atoms anisotropically refined is 0.094 for 1075 visually estimated intensities. The molecule is slightly but significantly non-planar. The structure is stabilized mainly by van der Waals interactions; however, a short Br$\cdots$O contact of length 3.298 Å, which is slightly less than the expected van der Waals separation, suggests that weak charge transfer interaction may be present. The C–Br$\cdots$O angle is 176.1°.

Introduction

The reaction between diazomethane and benzonitrile oxide in ether gives a light-yellow crystalline product

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with chemical formula $C_9N_3OH_9$. From nuclear magnetic resonance (n.m.r.) and ultraviolet spectra of this compound, three possible structures, shown in Fig. 1, were proposed although structure III was considered to be less likely than the other two (Nagarajan, 1965; Nagarajan & Rajagopalan, 1967). It seemed worthwhile to carry out an X-ray analysis to establish the

molecular structure. The *p*-bromo derivative was kindly supplied by Dr K. Nagarajan, CIBA Research Centre, Bombay, India.

Experimental

The crystals were yellow in colour with a needle-like shape. The unit-cell dimensions were determined from Weissenberg photographs taken around the *a* and *b* axes, standardized by copper powder lines ($a_0 = 3.615$ Å). The angle β was determined from a precession photograph of the $h0l$ net. The crystal data are given in Table 1. The density was determined by flotation in a mixture of bromoform and benzene.
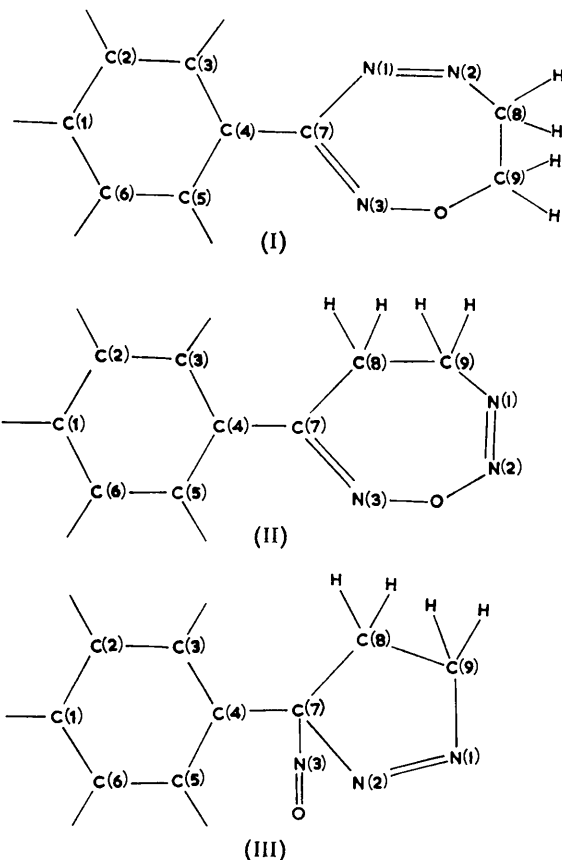

(I)

(II)

(III)

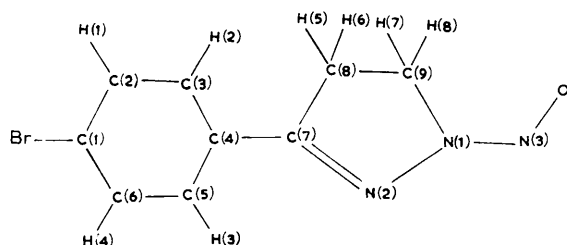Fig. 1. Possible structures suggested from other physical methods.

Fig. 2. The numbering of atoms in the structure.

Table 1. *Crystal data*

Crystal system	Monoclinic
Unit-cell dimensions	$a = 5.636 \pm 0.012$ Å
	$b = 9.775 \pm 0.021$
	$c = 17.516 \pm 0.031$
	$\beta = 97.4 \pm 0.2°$
Space group	$P2_1/c$ ($h0l$ absent for
	$l = 2n+1$; $0k0$
	absent for $k =$
	$2n+1$)
Contents of the unit cell	$4(C_9N_3OH_8Br)$
F.W.	254.1
$F(000)$	504
Observed density	1.78 g.cm^{-3}
Calculated density	1.76 g.cm^{-3}
μ(Cu $K\alpha$)	62.1 cm^{-1}

The diffraction data for layer lines 0 to 4 about the *a* and *b* axes were collected by the multiple-film equi-inclination technique using Cu $K\alpha$ radiation. Two crystals of cross section approximately 0.15×0.15 mm were used to collect the intensity data. The intensities were estimated visually by comparison with a calibrated scale. Corrections were applied for the Lorentz and polarization factors, and for the non-equatorial layers the Phillips (1954) correction factor. No correction for absorption was applied. The approximate scale factor for each layer 0 to 4 about the *a* axis was obtained by Wilson's (1942) method.

Structure determination and refinement

From the Patterson projections calculated using $0kl$ and $h0l$ reflexions the bromine was located at the position $x = 0.25$, $y = 0.0$, $z = 0.125$. With the heavy atom at $y = 0.0$ and $z = 0.125$, the electron density map calculated on the basis of signs derived from bromine contributions to the $0kl$ reflexions contained false symmetry elements because the bromine contributions were systematically zero for $k + l = 2n+1$ reflexions. After testing and rejecting several structures, two-dimensional work was given up. A three-dimensional electron density map, based on the signs of the bromine atom, and a three-dimensional weighted β synthesis (Ramachandran & Raman, 1959), were computed. In these calculations, only reflexions for which $|F_{Br}|$ was greater than $0.25 |F_o|$ were used. The coefficients used in computing the weighted β synthesis were $w^2|F_N|^2/F_{Br}^*$

where $w = \tanh [\sum|F_H| \, |F_{Br}|/\sum f_Q^2]$ (Woolfson, 1956). With $y_{Br} = 0.0$, the contributions of the bromine were zero for reflexions with $k + l = 2n+1$. Consequently a false *A* centring was introduced in both maps. None of the structures shown in Fig. 1 could explain the distribution of peaks. But a structure with a five-membered ring attached to the carbon atom C(4) in III (Fig. 1) with the nitroso group linked to atom N(1), instead of C(7), was derived from this map (Fig. 2). Both maps contained peaks at atomic sites, but the strength of the peaks for the unknown atoms were higher in the β-synthesis than in the Br-phased map. Structure factor

calculations with Br plus 13 light atoms gave an R value of 0·39 for the 936 observed reflexions collected down the a axis. At this stage of the investigation our attention was drawn to the paper by Vecchio, Crisafulli & Aversa (1966) who, from n.m.r. and chemical evidence, suggested for this yellow product a structure which agreed with the X-ray results, and they identified the compound as 1-nitroso-3-phenyl-2-pyrazoline.

Full-matrix least-squares refinements were carried out on the CDC-3600 computer at Bombay using the program written by Gantzel, Sparks & Trueblood (1961). The quantity minimized was $\sum w[|F_o| - k|F_c|]^2$. Two cycles of refinement with isotropic temperature factors, layer scale factors and unit weighting scheme were carried out. From a careful study of the $|F_o|$ vs. $\sum w\Delta F^2$ distribution the weighting scheme

$$w = \frac{1}{a + |F_o| + b|F_o|^2}$$

with $a = 6·0$ and $b = 0·02$, was chosen. Two cycles of refinement with this weighting scheme, treating bromine alone anisotropically, were performed. The R index decreased to 0·097. A difference Fourier synthesis was computed; it contained the peaks with heights ranging from 0·3 to 0·6 e.$Å^{-3}$ near the positions where the hydrogen atoms were expected to occur. In the subsequent structure factor calculations the contributions of the hydrogen atoms were included ascribing the same isotropic temperature factor of 3·5 $Å^2$ to all the hydrogen atoms. Their positional coordinates were obtained from geometrical considerations taking C–H lengths to be 1·1 Å.

At this stage about 150 reflexions were added to the $|F_o|$ list from the data collected about the b axis. These additional reflexions were placed on the same scale using the individual scale factors obtained for the layers $h = 0$ to 4 ($0kl$ to $4kl$) at the end of the least-squares calculations in which the isotropic thermal parameters were refined. Two cycles of refinement using anisotropic thermal parameters for all non-hydrogen atoms and refining the overall scale factor resulted in an R index of

0·094 for the 1075 observed reflexions. The shifts in the various parameters during the last cycle were less than $\frac{1}{10}$ their estimated standard deviations. The form factors for C, N, O and H atoms were taken from *International Tables for X-ray Crystallography* (1962) and for bromine the scattering factors of Thomas & Umeda (1957) were used, taking into account the real part ($\Delta f'_{Br} = -1·0$ for Cu $K\alpha$ radiation) of the anomalous dispersion corrections. The final atomic coordinates are given in Table 2. The anisotropic temperature factors of all the non-hydrogen atoms are given in Table 3. It must be emphasized that any extensive discussion of anisotropic thermal motion is not warranted as the initial scale factors for the layers $h = 0$ to 4 ($0kl$ to $4kl$) were determined individually by Wilson's (1942) method. It is not possible to determine the layer scale factors by Wilson's method because of interaction with the anisotropic temperature factors and in our case the interaction would be with the vibration parameter b_{11} (Lingafelter & Donohue, 1966). The observed and calculated structure factors are listed in Table 4. Of the 382 unobserved reflexions, 43 were calculated to about 1·5 F_{min}. The reflexions too weak to be observed were assigned an intensity of $I_{min}/3$ (Hamilton, 1955).

Table 2. *Final fractional atomic coordinates of the non-hydrogen atoms*

Standard deviations in the last digits are given in parentheses.

	x	y	z
Br	0·24229 (27)	−0·01820 (15)	0·12423 (8)
C(1)	0·1251 (21)	−0·1517 (12)	0·0529 (6)
C(2)	0·2462 (20)	−0·1759 (13)	−0·0108 (7)
C(3)	0·1645 (20)	−0·2712 (13)	−0·0670 (7)
C(4)	−0·0493 (19)	−0·3429 (12)	−0·0601 (6)
C(5)	−0·1724 (20)	−0·3178 (13)	0·0050 (7)
C(6)	−0·0864 (22)	−0·2235 (14)	0·0594 (7)
C(7)	−0·1389 (18)	−0·4387 (12)	−0·1209 (7)
C(8)	−0·0215 (23)	−0·4599 (13)	−0·1920 (7)
C(9)	−0·1796 (20)	−0·5682 (14)	−0·2367 (7)
N(1)	−0·3641 (17)	−0·5879 (11)	−0·1848 (6)
N(2)	−0·3402 (21)	−0·5100 (10)	−0·1168 (6)
N(3)	−0·5483 (19)	−0·6688 (11)	−0·1959 (8)
O	−0·5548 (16)	−0·7329 (10)	−0·2596 (6)

Table 3. *Anisotropic thermal parameters and their estimated standard deviations* *

The b_{ij}'s are defined by $T = \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\right]$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Br	4908 (65)	1394 (19)	350 (5)	−412 (50)	47 (24)	75 (17)
C(1)	425 (45)	114 (14)	31 (4)	−59 (40)	8 (20)	−7 (12)
C(2)	396 (44)	122 (15)	37 (5)	11 (39)	14 (22)	0 (13)
C(3)	362 (43)	123 (16)	42 (5)	−38 (37)	51 (22)	−11 (13)
C(4)	332 (39)	111 (14)	37 (5)	−58 (35)	45 (20)	−20 (12)
C(5)	390 (42)	127 (16)	36 (5)	−118 (40)	55 (21)	−35 (13)
C(6)	441 (49)	149 (17)	31 (5)	−15 (46)	31 (23)	−4 (14)
C(7)	243 (34)	114 (14)	41 (5)	−17 (34)	10 (18)	−9 (12)
C(8)	473 (53)	138 (17)	40 (5)	−25 (44)	86 (25)	2 (14)
C(9)	328 (42)	142 (16)	49 (5)	45 (40)	77 (23)	5 (15)
N(1)	417 (39)	116 (13)	42 (4)	−34 (36)	18 (19)	8 (12)
N(2)	511 (45)	114 (13)	39 (4)	−74 (36)	49 (20)	−8 (12)
N(3)	427 (42)	131 (15)	61 (6)	69 (40)	44 (24)	0 (15)
O	486 (39)	160 (14)	57 (5)	38 (34)	−22 (21)	4 (13)

* The values for Br are multiplied by 10^5 and for other atoms by 10^4.

Discussion

The bond lengths and bond angles involving the non-hydrogen atoms with their standard deviations are given in Table 5. The phenyl ring in the molecule has dimensions in agreement with the standard values. The variations in bond lengths $C(7)=N(2)$, $N(1)-N(2)$, $N(1)-N(3)$ and $N(3)-O$ from pure single and double bonds show that there is delocalization of π-electrons in the nitrosopyrazoline group. Furthermore the $C(4)-C(7)$ length of $1\cdot459$ Å is significantly shorter than the value $1\cdot507$ measured in biphenyl (Trotter,

1961). A similar variation in bond lengths within the pyrazoline ring and shortening of the bond length connecting the pyrazoline and phenyl rings was observed in the structure of diphenyl-Δ^2-pyrazoline (Duffin, 1968). These variations in bond lengths from pure single and double bonds can be explained if one considers the possible resonance structures or the predictions of the simple Hückel molecular orbital (HMO) theory. The π-bond orders were determined from the HMO theory for the present structure and the results, along with the constants used, are listed in Table 6. The π-bond order of $0\cdot473$ for the $C(4)-C(7)$ bond shows

Table 4. *Observed and calculated structure factors*

Table 5. *Bond lengths and angles with their standard deviations given in parentheses*

Br——C(1)	1·867 (12) Å	Br——C(1)—C(2)	118·9 (1·0)°
C(1)–C(2)	1·401 (17)	Br——C(1)—C(6)	121·8 (1·0)
C(1)–C(6)	1·401 (17)	C(1)–C(2)–C(3)	121·8 (1·3)
C(2)–C(3)	1·390 (17)	C(2)–C(3)–C(4)	118·7 (1·3)
C(3)–C(4)	1·413 (16)	C(3)–C(4)–C(5)	119·3 (1·2)
C(4)–C(5)	1·430 (16)	C(4)–C(5)–C(6)	120·4 (1·2)
C(4)–C(7)	1·459 (16)	C(5)–C(6)–C(1)	120·6 (1·3)
C(5)–C(6)	1·369 (18)	C(6)–C(1)–C(2)	119·2 (1·2)
C(7)–C(8)	1·498 (17)	C(3)–C(4)–C(7)	118·4 (1·2)
C(7)–N(2)	1·341 (16)	C(5)–C(4)–C(7)	122·3 (1·2)
C(8)–C(9)	1·532 (18)	C(4)–C(7)–C(8)	123·2 (1·2)
C(9)–N(1)	1·479 (16)	C(4)–C(7)–N(2)	120·7 (1·2)
N(1)–N(2)	1·405 (15)	C(7)–C(8)–C(9)	103·3 (1·2)
N(1)–N(3)	1·300 (16)	C(8)–C(9)–N(1)	100·6 (1·2)
N(3)–O	1·276 (15)	C(9)–N(1)–N(2)	116·9 (1·1)
		N(1)–N(2)–C(7)	103·0 (1·1)
		N(2)–C(7)–C(8)	116·1 (1·2)
		C(9)–N(1)–N(3)	126·8 (1·1)
		N(2)–N(1)–N(3)	116·4 (1·1)
		N(1)–N(3)–O	111·2 (1·2)

Table 6. *Results of the molecular orbital calculations for 3-p-bromophenyl-1-nitroso-2-pyrazoline*

Bond	Constant k^*	π-bond order	Atom	Constant h^*	π-charge
Br——C(1)	0·3	0·117	Br	1·5	0·014
C(1)–C(2)	1·0	0·649	C(1)	0·0	0·038
C(1)–C(6)	1·0	0·649	C(2)	0·0	−0·007
C(2)–C(3)	1·0	0·687	C(3)	0·0	0·032
C(3)–C(4)	1·0	0·587	C(4)	0·0	−0·010
C(4)–C(5)	1·0	0·587	C(5)	0·0	0·032
C(4)–C(7)	1·0	0·473	C(6)	0·0	−0·007
C(5)–C(6)	1·0	0·687	C(7)	0·0	0·146
C(7)–N(2)	0·8	0·768	N(1)	1·5	0·500
N(1)–N(2)	1·0	0·419	N(2)	0·5	−0·200
N(1)–N(3)	1·0	0·673	N(3)	0·5	0·163
N(3)–O	0·7	0·585	O	1·5	−0·698

* The constants h and k which are related to the Coulomb (α) and resonance (β) integrals of the atoms are defined by $\alpha = \alpha_0 + h\beta_0$ and $\beta = k\beta_0$, where α_0 and β_0 are the Coulomb and resonance integrals respectively for the carbon atom in the benzene ring.

that there is delocalization of π-electrons between the two rings.

In this connexion it was noticed that the π-bond order–length relationship for N–N bonds has not been established as in the case of C–C and C–N bonds (Coulson, 1959; Herbstein & Schmidt, 1955; Bertinotti, Giacomello & Liquori, 1956; Donohue, Lavine & Rollett, 1956). In order to obtain an order–length curve for N–N bonds, molecular orbital calculations using simple HMO method were carried out for the structures (Table 7) containing N–N bonds with partial double-bond character, and for which fairly accurate bond lengths are known from structural studies. The constants used in these calculations are close to those given by Streitwieser (1961). The N–N bond distances measured in these molecules were plotted against the corresponding π-bond orders as shown in Fig. 3. If the relationship between bond order and bond length is assumed to be linear, these points, when extrapolated, give values of 1·26 and 1·46 Å for the N–N double and single bonds respectively. The accepted values for the N–N double and single bonds are 1·24

and 1·44 Å (*International Tables for X-ray Crystallography*, 1962).

Table 7. *Structures used for drawing the order–length curve for the N–N bond and the corresponding references*

Serial number	Compound	Reference
1	3-p-Bromophenyl-1-nitroso-2-pyrazoline	Present study
2	Diphenyl-Δ^2–pyrazoline	Duffin (1968)
3	Pyrazole	Ehrlich (1960)
4	Nitrosodimethylamine	Rademacher, Stolevik & Lüttke (1968)
5	Nitroguanidine	Bryden, Burkardt, Hughes & Donohue (1956)
6	S-tetrazine	Bertinotti, Giacomello & Liquori (1956)
7	Antipyrine perchlorate	Vijayan & Viswamitra (1968)

It is of interest to compare the features of the pyrazoline ring as determined in different structures.

Table 8 lists the observed bond lengths and bond angles in the pyrazoline ring in (i) diphenyl-Δ^2-pyrazoline (Duffin, 1968), (ii) pyrazoline hydrochloride (Nardelli & Fava, 1962) and (iii) 1-p-iodophenyl-3-phenyl-pyrazoline adduct of isocolumbin (Cheung, Melville, Overton, Robertson & Sim, 1966). The bond lengths and bond angles in the pyrazoline ring of the present study have also been included in this Table.

The following interesting observations have been made from this comparative analysis. The C(8)–C(9) distance in the present structure, diphenyl-Δ^2-pyrazoline and 1-p-iodophenyl-3-phenyl pyrazoline agree

Fig. 3. Curve showing the variation of bond length with bond order for N–N bonds. 1, 2, 3 etc. refer to the structures listed in Table 7.

quite well, with an average value 1·528 Å. However in the case of pyrazoline hydrochloride this length is short (1·472 Å) and the authors (Nardelli & Fava, 1962) attribute this shortening to hyperconjugation effects. Of further interest is the observation that the C(7)–C(8) length is shorter than the C(8)–C(9) length in the present structure as well as in diphenyl-Δ^2-pyrazoline. This shortening of C(7)–C(8) may be due to the fact that it is a bond between sp^2 and sp^3 hybridized carbon atoms.

In the case of pyrazoline hydrochloride and 1-p-iodophenyl-3-phenyl-pyrazoline the C(7)=N(2) and N(1)–N(2) lengths appear to be pure double and single bonds respectively, without any resonance. But in the case of diphenyl-Δ^2-pyrazoline and the present study these bond lengths vary from their pure single or double bond lengths. Finally, the bond angles in the pyrazoline ring vary as we go from one structure to the other which may be due to the different amount of double bond character possessed by the C(7)–N(2) and N(1)–N(2) bonds in these structures.

In the case of $\rangle$N(1)–N(3)–O, N(1)–N(3) and N(3)–O bond lengths of 1·300 and 1·276 Å respectively agree with the values of 1·30 and 1·25 Å observed in the structure of 1-(4-chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazole)hydrazine in which this group occurs (Palenik, 1965).

Owing to the double-bond character possessed by the bonds C(4)–C(7), N(1)–N(2) and N(1)–N(3) one may expect the molecule to be planar. The deviations of the atoms from the least-squares plane passing through all the non-hydrogen atoms (Table 9) show that the molecule is clearly non-planar. Since $\chi^2 = \sum \Delta^2/\sigma^2 = 75$, the non-planarity must be regarded as highly significant (Fisher & Yates, 1957). The benzene ring is planar with $\chi^2 = 7\cdot8$. It is interesting to observe that the deviations of bromine and the atoms belonging to the nitroso-
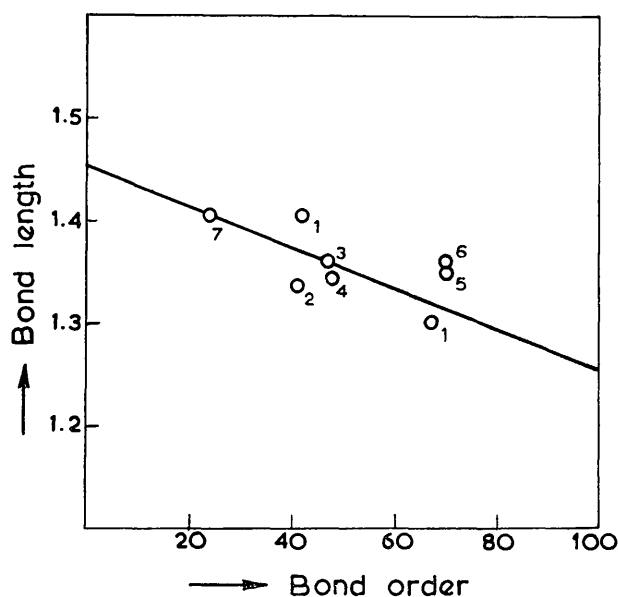
Table 8. *Bond lengths and angles of the pyrazoline ring as observed in various structures*

Bond	Present study	Diphenyl-Δ^2-pyrazoline	Pyrazoline hydrochloride	1-p-Iodophenyl-3-phenyl-pyrazoline
C(7)–C(8)	1·498Å	1·488Å	1·473Å	1·524 Å
C(7)–N(2)	1·341	1·333	1·255	1·275
C(8)–C(9)	1·532	1·521	1·472	1·531
C(9)–N(1)	1·479	1·493	1·498	1·437
N(1)–N(2)	1·405	1·336	1·468	1·451
Standard deviation	0·016	0·007	0·009	0·020
Angle				
C(7)–C(8)–C(9)	103·3°	102·4°	102·5°	103·0°
C(8)–C(9)–N(1)	100·6	102·7	105·5	102·5
C(9)–N(1)–N(2)	116·9	112·1	107·7	113·3
N(1)–N(2)–C(7)	103·0	109·4	106·9	106·6
N(2)–C(7)–C(8)	116·1	112·6	117·4	114·2
Standard deviation	1·2	0·5	0·6	1·2

pyrazoline group are significant and are on the same side of the least-squares plane through the phenyl ring (Table 9). Furthermore, it is found that atoms farthest from the C(4)–C(7) bond in the direction of the pyrazoline ring are displaced more than the atoms closer to it. Thus the molecule is very slightly, but significantly bow shaped, the distortion involving a bending about C(4)–C(7) and C(1)–Br bonds. Apart from these out-of-plane displacements there also seems to be a small rotation about C(4)–C(7). The reason for the non-planarity seems to be due to intramolecular and intermolecular effects. The intermolecular effect will be dealt with at the end, where the packing of the molecule is discussed.

Owing to the partial double-bond character of the N(1)–N(2) and N(1)–N(3) bonds, the atoms C(8) and C(9) would be expected to lie in the plane through atoms C(7), N(1), N(2), N(3) and O. It is found from

Table 9. *Least-squares planes*

The equation to the plane is $AX + BY + CZ = D$ with respect to the crystallographic axes a, b and c^* where X, Y, Z are in Å.

|	Plane I	Plane II	Plane III	Plane IV
Br	−0·096*	−0·062	—	—
C(1)	0·002*	0·004*	—	—
C(2)	0·020*	−0·005*	—	—
C(3)	0·056*	0·006*	—	—
C(4)	0·044*	−0·005*	—	—
C(5)	0·025*	0·003*	—	—
C(6)	−0·006*	−0·003*	—	—
C(7)	0·027*	−0·048	0·001*	0·017*
C(8)	−0·041*	−0·145	−0·034	−0·005*
C(9)	−0·032*	−0·156	−0·005*	−0·012*
N(1)	0·003*	−0·100	0·005*	0·028*
N(2)	0·025*	−0·049	−0·006*	−0·030*
N(3)	0·001*	−0·108	0·006*	—
O	−0·040*	−0·176	−0·005*	—
Equation to the plane				
A	0·476	0·471	0·484	0·525
B	−0·727	−0·718	−0·736	−0·719
C	0·495	0·513	0·474	0·455
D	1·809	1·808	1·915	1·883

* Atoms included for defining the plane
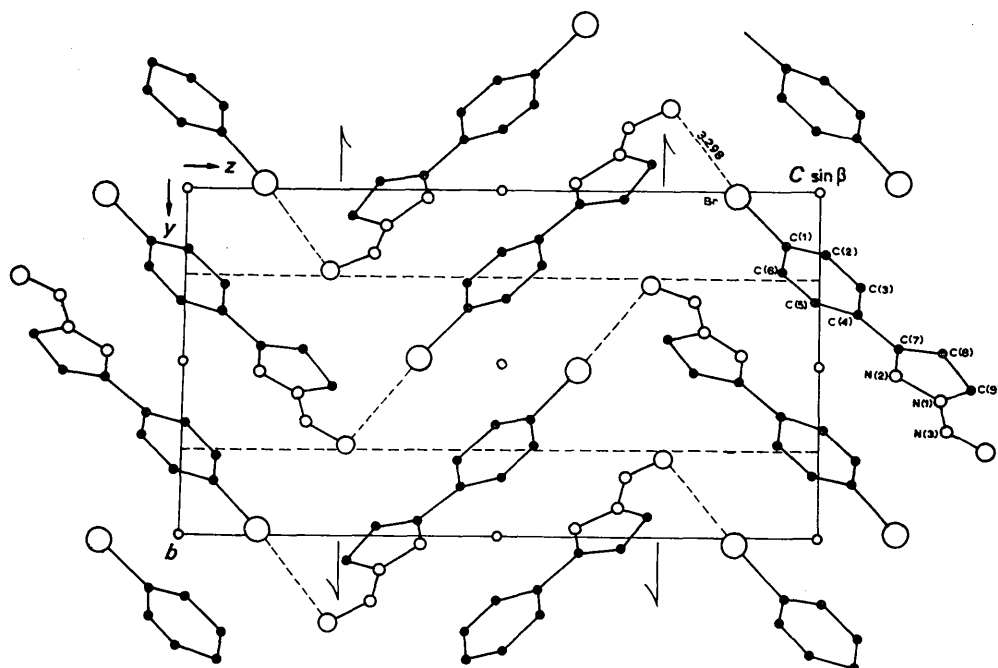
Fig. 4. View of the structure projected down the a axis.

Table 9 that while C(9) lies on this plane, C(8) deviates by a small amount (0·034 Å). This may probably be due to intramolecular overcrowding; for example, the distance H(2) to C(8) of 2·551 Å is shorter than the sum of the van der Waals radii of 2·8 Å for C···H. A similar effect has also been observed in diphenyl-Δ^2-pyrazoline (Duffin, 1968).

The view of the structure down the a axis is shown in Fig. 4. The only intermolecular contact less than the sum of the van der Waals radii of atoms is between Br and O (3·298 Å). All other contacts correspond to normal van der Waals interactions. The short contact between Br and O which is slightly but significantly less than the sum of the van der Waals radii (3·35 Å) could be due to weak charge-transfer interaction in the crystal as found, for example, in oxalyl bromide (Groth & Hassel, 1962) and in N-(p-bromophenyl)sydnone (Bärnighausen, Jellinek, Munnik & Vos, 1963). In this connexion it is noteworthy that the C–Br···O in the present structure is linear (176·1°) as in oxalyl bromide (169°) and sydnone (163·2°).

As mentioned earlier, the non-planarity of the molecule can be explained in terms of a bending about C(4)–C(7) and C(1)–Br bonds. In order to verify whether this could be due to intermolecular effects the following calculations were performed. The bromine and the atoms C(7), N(1), N(2), N(3) and O were brought to the plane passing through the phenyl ring. It is interesting to note that the intermolecular distance between Br and O calculated using the positional coordinates corresponding to the planar molecule has increased to 3·457 Å which is 0·1 Å more than the sum of the van der Waals radii. From this it appears that the non-planar molecule seems to facilitate the charge-transfer interaction more than the planar molecule.

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