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The Crystal and Molecular Structure of Erythristemine 2-Bromo-4,6-dinitrophenolate

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The structure of the 2-bromo-4,6-dinitrophenolate of a new naturally occurring aromatic erythrina alkaloid has been determined by conventional X-ray crystallographic methods and refined to $R=0{\cdot}071$. The derivative crystallizes in the monoclinic space group $P2_1$ with $a=7{\cdot}998$, $b=16{\cdot}159$, $c=10{\cdot}550$ Å and $\beta=97{\cdot}48°$; $Z=2$. The absolute configuration was found to be $3R,5S,11S$, thus confirming the theory of a common biosynthetic origin for the erythrina alkaloids. The nature of the 2-bromo-4,6-dinitrophenolate anion is discussed. The crystal packing was found to be partly attributable to π–π charge-transfer effects.

Erythristemine is one of a series of curare active alkaloids which have been extracted from plants in the genus *Erythrina* (Mondon, 1970). Broadly speaking they fall into two classes, the aromatic erythrina alkaloids [Fig. 1(*a*)] and the erythroidines [Fig. 1(*b*)]. The numbering scheme for the 'parent' hydrocarbon, erythrinane, is shown in Fig. 1(*c*). The proposed structure (Carmack, McCusick & Prelog, 1951) of the aromatic alkaloid erythraline [Fig. 1(*a*), $R_1,R_2=CH_2$, $R_3=CH_3$] was confirmed by the determination of the crystal structure of its hydrobromide (Nowacki & Bonsma, 1958) and that of β-erythroidine by the determination of the crystal structure of the hydrobromide of dihydro-β-erythroidine (Hanson, 1963). More recently a crystallographic study of the alkaloid cocculine has shown that it and its congener cocculolidine are also aromatic erythrina alkaloids (Razakov & Yunusov, 1970). The structure of cocculine is shown in Fig. 1(*d*).

During the course of the studies which established a common biosynthetic pathway for the erythrina alkaloids, attempts were made (Barton, Jenkins, Letcher, Widdowson, Hough & Rogers, 1970; Barton, Boar & Widdowson, 1970) to extract erythraline from a new erythrina species, *Erythrina lysistemon*. A non-polar alkaloid was obtained which, after purification, gave a crystalline solid, m.p. 127–129 °C, which was named erythristemine. Microanalysis, combined with mass spectroscopy, gave the formula $C_{20}H_{25}NO_4$. The spectroscopic properties of the compound were almost identical with those of erythraline and the mass spectroscopic breakdown pattern was consistent with an aromatic erythrina alkaloid having a 1,6-diene system and an additional oxygen function on either ring *C* or ring *D*. Extensive n.m.r. studies (Barton *et al.*, 1970) showed that the oxygen function was located on ring *C* but were unable to identify its exact position or the configuration of this ring.

In view of the biological importance of curare compounds but of the limited information available by spectroscopic techniques, it was decided to attempt an X-ray study. This would also reveal the absolute configuration of the aromatic erythrina alkaloids and relate them to the erythroidines. The result is shown in Fig. 1(*e*).

Excellent crystals of the 2-bromo-4,6-dinitrophenolate were obtained from ethyl alcohol as thin hexagonal plates elongated along **a** and with (001) prominent. They showed sharp extinction parallel to **a**. A photographic examination showed that the crystals had $2/m$ Laue symmetry and the absent spectra $0k0$, $k=2n$, combined with the known optical activity, uniquely determined the space group as $P2_1$. The density of the compound was measured by flotation in an aqueous solution of potassium iodide.

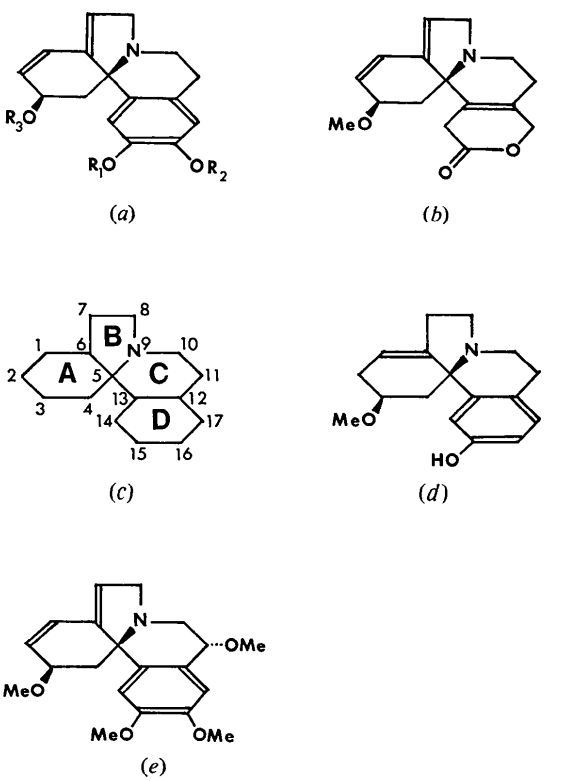


Fig. 1. Molecular formulae.

Crystallographic data

($C_{20}H_{25}NO_4.C_6H_3N_2O_5Br$): $M=606{\cdot}45$, m.p. 144–148 °C, monoclinic, $a=7{\cdot}998$ (3), $b=16{\cdot}159$ (5), $c=10{\cdot}550$ (5) Å, $\beta=97{\cdot}48$ (1)°, $U=1352$ Å^3, $D_m=1{\cdot}50$ (1), $D_c=1{\cdot}49$ g cm^{-3}, for $Z=2$, space group $P2_1$, $F(000)=624$, μ(Cu $K\alpha$ radiation) $=29{\cdot}5$ cm^{-1}.

Intensity data for 2086 independent reflexions were collected on a Siemens automatic single-crystal diffractometer operated in the coupled θ–2θ mode out to $\theta=60°$. The reference reflexion (0,10,0) showed no significant decline in intensity during the five days of the data collection. The raw data were processed in the normal manner (Allen, Rogers & Troughton, 1971) and of the 2086 reflexions examined, 2044 were classified as significantly above the background radiation level [*i.e.* $I>2{\cdot}58\sigma(I)$].

The structure was solved by the heavy-atom method and, after absorption correction, was refined to an R value of 0·082. 24 H atoms were located in difference Fourier maps and the remaining four were included in calculated positions to give a final R of 0·071. The structural asymmetric unit and the atomic numbering scheme are shown in Fig. 2. Tables 1 and 2 contain the positional parameters of the non-hydrogen atoms and the H atoms respectively.*

* A list of structure factors and thermal parameters has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31364 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

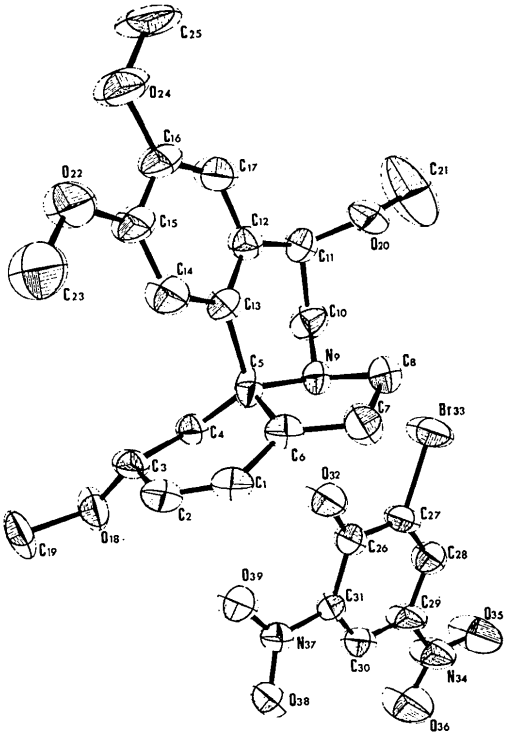


Fig. 2. The structural asymmetric unit.

Table 1. *Positions of the non-hydrogen atoms in fractional coordinates* $\times 10^4$ *(standard deviations in parentheses)*

	x	*y*	*z*
C(1)	2223 (14)	5142 (7)	8288 (11)
C(2)	3842 (15)	5280 (6)	8520 (11)
C(3)	5139 (13)	5015 (8)	7785 (9)
C(4)	4407 (13)	4709 (6)	6405 (9)
C(5)	2841 (12)	4226 (7)	6432 (9)
C(6)	1590 (14)	4663 (6)	7133 (10)
C(7)	4 (14)	4613 (8)	6522 (11)
C(8)	3 (15)	4130 (7)	5308 (11)
N(9)	1830 (11)	4174 (5)	5093 (8)
C(10)	2427 (15)	3525 (8)	4211 (11)
C(11)	2337 (15)	2630 (7)	4709 (11)
C(12)	2977 (13)	2609 (7)	6141 (10)
C(13)	3119 (14)	3286 (7)	6917 (10)
C(14)	3673 (16)	3163 (8)	8254 (10)
C(15)	4145 (17)	2420 (7)	8698 (11)
C(16)	3994 (17)	1736 (7)	7886 (12)
C(17)	3406 (17)	1841 (7)	6629 (12)
O(18)	6400 (10)	5563 (5)	7578 (8)
C(19)	7518 (15)	5761 (9)	8757 (11)
O(20)	650 (11)	2351 (5)	4566 (8)
C(21)	88 (28)	2031 (16)	3370 (19)
O(22)	4762 (15)	2239 (5)	9950 (9)
C(23)	4851 (26)	2894 (11)	1086 (13)
O(24)	4502 (14)	980 (5)	8452 (9)
C(25)	4327 (26)	239 (7)	7654 (17)
C(26)	1855 (15)	6251 (7)	3392 (11)
C(27)	972 (16)	6097 (7)	2133 (11)
C(28)	628 (16)	6693 (7)	1201 (12)
C(29)	1174 (18)	7477 (7)	1500 (12)
C(30)	2044 (16)	7679 (7)	2659 (11)
C(31)	2346 (13)	7099 (6)	3591 (10)
O(32)	2114 (13)	5671 (5)	4209 (8)
Br(33)	342 (2)	5000 (0)	1712 (1)
N(34)	854 (17)	8102 (7)	488 (10)
O(35)	−37 (19)	7931 (6)	−479 (9)
O(36)	1524 (18)	8788 (6)	714 (11)
N(37)	3246 (12)	7343 (5)	4801 (9)
O(38)	3856 (13)	6840 (5)	5580 (8)
O(39)	3386 (11)	8093 (5)	5019 (8)

Table 2. *Positions of the hydrogen atoms in fractional coordinates* $\times 10^3$

Each hydrogen atom is given the number of the carbon atom to which it is bonded. Atoms marked with an asterisk are shown with calculated coordinates (see text).

	x	*y*	*z*
H(1)	132	528	890
H(2)	416	572	907
H(3)	552	452	803
H(4*A*)	528	450	593
H(4*B*)	440	504	576
H(7)	868	488	673
H(8*A*)	942	460	450
H(8*B*)	964	350	547
H(9)*	195	478	473
H(10*A*)	140	368	333
H(10*B*)	384	380	400
H(11)	348	234	420
H(14)	380	372	883
H(17)	328	148	623
H(19*A*)	768	504	873
H(19*B*)	672	598	960
H(19*C*)	912	552	860
H(21*A*)	868	180	367
H(21*B*)	133	220	263

Table 2 (*cont.*)

H(21*C*)*	−22	177	251
H(23*A*)	558	280	173
H(23*B*)	360	340	80
H(23*C*)*	484	262	1171
H(25*A*)	480	984	817
H(25*B*)	340	8	683
H(25*C*)	520	16	680
H(28)*	0	656	34
H(30)	224	804	273

The absolute configuration

The absolute configuration of the compound was determined by visual comparison of a selected set of Bijvoet pairs. The relevant reflexions in space group $P2_1$ are hkl or $\bar{h}kl$ *versus* $h\bar{k}l$ or $\bar{h}\bar{k}\bar{l}$. The intensities of a set of $hk0$, $h\bar{k}0$ pairs were calculated and the sign of the intensity differences is compared with the observed difference below.

h	*k*	*l*	Calculated	Observed
6	3	0	+	−
2	4	0	−	+
5	4	0	−	+
1	5	0	−	+
2	5	0	−	+
3	5	0	−	+
5	5	0	−	+
7	5	0	−	−
1	6	0	−	+
2	6	0	−	+
1	7	0	−	+
2	7	0	−	+
4	7	0	+	−
5	7	0	+	−
7	7	0	−	+
6	5	0	+	−
4	5	0	+	−
5	6	0	+	−
6	6	0	+	−
8	1	0	−	+

This shows clearly that the absolute configuration is the opposite of that used for the structure determination. However, the atomic coordinates and diagrams in this paper conform to the correct absolute configuration.

Results and discussion

In accordance with the chemical and spectroscopic evidence, erythristemine was found to be a new aromatic erythrina alkaloid. It is the first known naturally occurring tetramethoxylated erythrina alkaloid, its nearest homologue being the trimethoxylated alkaloid derivative erysotrine (Fig. 1, R_1, R_2 and R_3=Me). Erythristemine carries its additional methoxy group in the 11 position and the presence of this group introduces a third asymmetric centre. The configurations of the three asymmetric centres are 3*R*,5*S*,11*S*, thus confirming the assumption that the 3*R*,5*S* configuration of the erythroidines also occurs in the aromatic erythrina alkaloids. This result confirms the theory of a common biosynthetic origin for the two types of erythrina alkaloid.

In the subsequent discussion of the molecular structure of the compound the following abbreviations will be adopted for the structures examined by X-rays: erythristemine ERTE, erythraline ERTA, β-dihydroerythroidine HERTO, cocculine COCC, and the 2-bromo-4,6-dinitrophenolate moiety will be referred to as 2BDNP.

The molecule contains the expected tetracyclic erythrinan skeleton and is essentially similar in shape to ERTE and COCC. This similarity is enforced by the fusion of the *A*/*B* bicyclic ring system with the *C*/*D* ring system at the alkaloidal nitrogen atom [N(9)] and the spiro atom [C(5)]. In ERTE rings *C* and *D* form a plane which lies at 84° to the best plane through rings *A* and *B*. In ERTA this angle is 88° but in HERTO the angle is 69°, reflecting the considerable difference between the latter molecule and the aromatic erythrina alkaloids.

The 2BDNP moiety lies beneath the plane of rings *A* and *B*, in a plane rotated some 20° out of that through rings *C* and *D*. The phenolic O atom lies 2·61 Å from the alkaloidal N atom, forming a short N···O hydrogen-bonded contact.

The bond lengths and angles in the structure, together with their standard deviations are shown in Figs. 3 and 4. On the whole these values are similar to those reported for ERTA, COCC and where relevant, HERTO. As no standard deviations were quoted for those structures, a detailed comparison of the individual bonds is difficult and the discussion will be restricted to common features.

(*a*) *The erythristemine moiety*

The most marked deviation from normal bond lengths in this molecule is that of the C(5)–C(13) bond (1·61 Å) which is some 10σ longer than the normal value for a C_{arom}–C_{sp3} bond. Table 3 contains the bond lengths and angles around C(5) in the four crystallographically determined erythrina alkaloids and it is plain from these data that in three cases, HERTO, ERTE and COCC, either the C(4)–C(5) bond or the C(5)–C(13) bond is longer than normal. The sum of the two lengths is in each of these cases 3·09 Å. In the fourth structure, ERTA, the effect seems to be shared between the two bonds and the sum of the two lengths is marginally higher (3·13 Å).

In the three structures where bond-angle data are available C(4)C(5)C(13) is the largest of the six angles around C(5) with a mean value of 114°. This is followed by C(4)C(5)C(6) (mean 112°). On the other hand, C(6)C(5)N(9) is considerably smaller than the normal tetrahedral angle with a mean value of 99°.

A second bond which deviates significantly from the normal value is the C_{sp3}–C_{sp2} single bond between C(2)

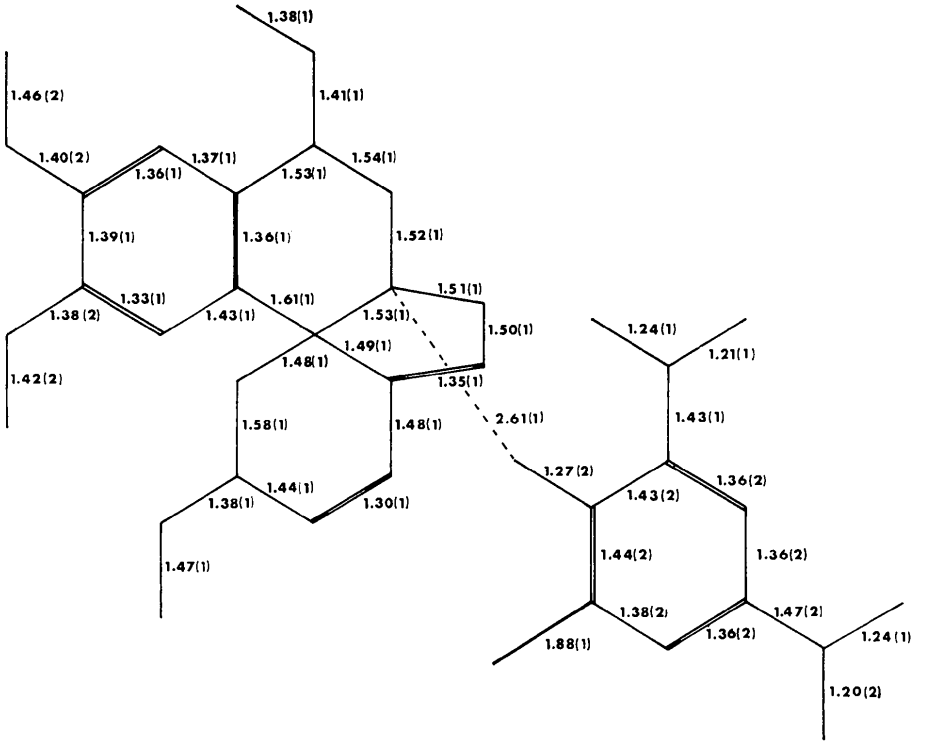


Fig. 3. The bond lengths (estimated standard deviations in parentheses).

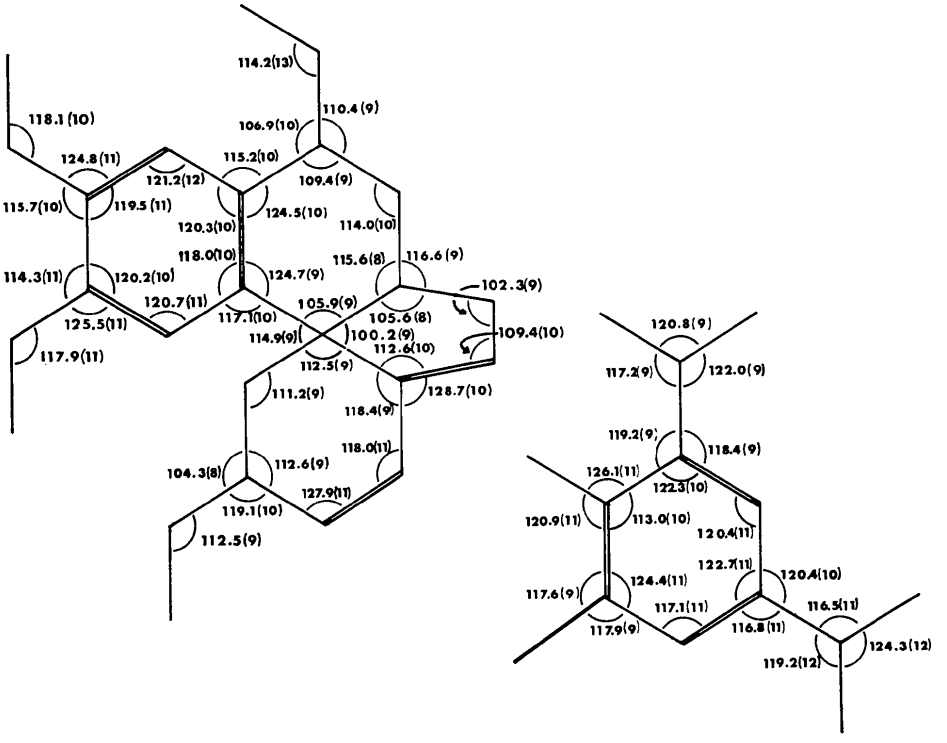


Fig. 4. The bond angles (estimated standard deviations in parentheses). For the two other angles at C(5) see Table 3.

Table 3. *Bond lengths* (Å) *and angles* (°) *around* C(5) *in the erythrina alkaloids*

Angle	Compound ERTE	ERTA	HERTO
C(4)–C(5)–C(6)	112·5	113	111
C(4)–C(5)–N(9)	110·9	109	110
C(4)–C(5)–C(13)	114·9	115	113
C(6)–C(5)–N(9)	100·1	100	98
C(6)–C(5)–C(13)	111·2	110	113
N(9)–C(5)–C(13)	105·9	108	110

Bond	ERTE	ERTA	HERTO	COCC
C(5)–C(4)	1·48	1·56	1·59	1·61
C(5)–C(6)	1·49	1·49	1·53	1·46
C(5)–N(9)	1·53	1·52	1·48	1·55
C(5)–C(13)	1·61	1·57	1·50	1·47

and C(3) [1·44 (1) Å] and the bonding system from C(2) through C(3), C(4) and C(5) to C(13) is therefore generally irregular with alternate long and short bonds. This tendency is also apparent in COCC and ERTA and together with opening of the C(4)–C(5)–C(13) valence angle (see Table 3) is probably due to repulsion forces between the H atom on C(14) and atoms in ring *A*.

Thus, it is clear from Fig. 2 that the fusion of the two 'planar' moieties (rings *A* and *B* and rings *C* and *D*) at C(5) and N(9) produces a situation where C(14) lies almost centrally over ring *A* and is close to all six atoms in that ring. In most cases the H atoms on ring *A* are directed away from that on C(14) but in one case [H(13)] this is not so and a close H···H contact (2·14 Å) occurs. This distance is significantly shorter than twice the mean van der Waals radius of H calculated by Bondi (1964) from a number of crystal structures (2·40 Å) and implies steric repulsion. This repulsion is reinforced by interactions between H(14) and both C(1) and C(2) (2·65 and 2·54 Å respectively) and is almost certainly responsible for the stretching of the C(5)–C(13) and C(13)–C(14) bonds, the shortening of the C(14)–C(15) bond and the decrease in the bond angle at C(13) from the 120° of a regular hexagon.

The two olefinic systems, C(6),(1),(2),(3) and C(5),(6),(7),(8) form a non-planar *trans* diene system with a torsion angle of 18° about the C(1)–C(6) bond and with C(1) lying 0·13 Å out of the plane through C(5),(6),(7),(8). The torsion angle about the C(1)–C(6) bond is similar to that about the same bond in ERTA (17·6°), the only other determined erythrina alkaloid containing the *trans* diene system. The three C_{sp3}–N bonds show the increase in length which arises on protonation of the N atom and are typical C_{sp2}–N^+ bonds (Birnbaum, 1967).

With the exception of the aromatic ring (*D*) and its substituents the rings in the structure are generally distorted from 'ideal' conformations. This arises from either the presence of double bonds or the effect of fusion with neighbouring rings. The deviations of the atoms from the best or most prominent plane in each ring are shown in Table 4, and Table 5 contains the torsion angles around the bonds in each ring.

Table 4. *Least-squares planes in the structure*

Planes are expressed in the form $Px+Qy+Rz-S=0$; x,y,z being the fractional coordinates of Table 1. Deviations of the atoms from the planes are tabulated in Å × 10^3. Atoms marked with an asterisk were not included in the calculations of the planes. The value shown with these atoms is their deviation from the planes through the other atoms.

(1) Ring *A* and the first olefin system

$P=-0·351$ $Q=13·770$ $R=-5·495$ $S=2·394$

C(1)	−2	C(5)*	−255
C(2)	2	C(7)*	322
C(3)	−1	N(9)*	444
C(6)	1	C(13)*	−1816
C(4)*	364	O(18)*	816
C(19)*	399		

(2) Ring *B* and the second olefin system

$P=1·686$ $Q=13·627$ $R=5·446$ $S=2·737$

C(5)	−1	C(4)*	935
C(6)	2	N(9)*	485
C(7)	−2	C(10)*	183
C(8)	1	C(13)*	−1450
C(1)	132		

(3) Ring *C*

$P=7·846$ $Q=1·1265$ $R=-3·187$ $S=0·642$

C(5)	13	N(9)*	−360
C(11)	−13	C(10)*	317
C(12)	30	C(14)*	−35
C(13)	−30	C(17)*	125
C(4)*	1305	O(20)*	−1322
C(6)*	−1427		

(4) Ring *D*

$P=7·756$ $Q=2·398$ $R=-3·307$ $S=0·903$

C(12)	1	C(5)*	187
C(13)	16	C(11)	−17
C(14)	−25	O(24)*	29
C(15)	16	C(25)*	−21
C(16)	3	O(22)*	37
C(17)	−11	C(23)*	−38

(5) The benzene ring in the 2BDNP moiety

$P=7·348$ $Q=-3·334$ $R=-4·754$ $S=-2·337$

C(26)	3	Br(33)*	108
C(27)	5	N(34)*	32
C(28)	−3	O(35)*	−107
C(29)	−6	O(36)*	187
C(30)	15	N(37)*	−8
C(31)	−14	O(38)*	237
O(32)*	1	O(39)*	−259
		N(9)*	−131

(*b*) *The* 2-*bromo*-4,6-*dinitrophenolate moiety*

Taken as a whole the 2BDNP moiety is approximately planar but the benzene ring itself is closely planar ($\sigma=0·01$ Å), see Table 4. Of the 'first' substituent atoms on the benzene ring, the Br atom is the most seriously out of plane (0·1 Å) but the nitro groups are rotated by approximately 13° and 7° about their C–N bonds [for C(29)–N(34) and C(31)–N(37) respectively]. The difference between the two O–N–O angles fits the approximately linear correlation between the length of the C–N bond and the O–N–O

Table 5. *The torsion angles* (°)

(1) Ring *A*		
	C(6)—C(1)—C(2)—C(3)	−0·5
	C(1)—C(2)—C(3)—C(4)	15·0
	C(2)—C(3)—C(4)—C(5)	−39·6
	C(3)—C(4)—C(5)—C(6)	50·2
	C(4)—C(5)—C(6)—C(1)	−37·7
	C(5)—C(6)—C(1)—C(2)	11·5
(2) Ring *B*		
	C(5)—C(6)—C(7)—C(8)	−0·4
	C(6)—C(7)—C(8)—N(9)	−18·9
	C(7)—C(8)—N(9)—C(5)	30·4
	C(8)—N(9)—C(5)—C(6)	−30·0
	N(9)—C(5)—C(6)—C(7)	19·1
(3) Ring *C*		
	C(5)—N(9)—C(10)—C(11)	61·4
	N(9)—C(10)—C(11)—C(12)	−42·8
	C(10)—C(11)—C(12)—C(13)	17·9
	C(11)—C(12)—C(13)—C(5)	−7·3
	C(12)—C(13)—C(5)—N(9)	19·2
	C(13)—C(5)—N(9)—C(10)	−44·7
(4) Ring *D*		
	C(12)—C(13)—C(14)—C(15)	4·7
	C(13)—C(14)—C(15)—C(16)	−4·6
	C(14)—C(15)—C(16)—C(17)	1·9
	C(15)—C(16)—C(17)—C(12)	0·8
	C(16)—C(17)—C(12)—C(13)	−0·6
	C(17)—C(12)—C(13)—C(14)	−2·0
(5) Torsion angles about the C–N bonds in the 2BDNP moiety		
	C(28)—C(29)—N(34)—O(35)	9·3
	C(30)—C(29)—N(34)—O(36)	5·5
	C(30)—C(31)—N(37)—O(38)	14·7
	C(26)—C(31)—N(37)—O(39)	12·8

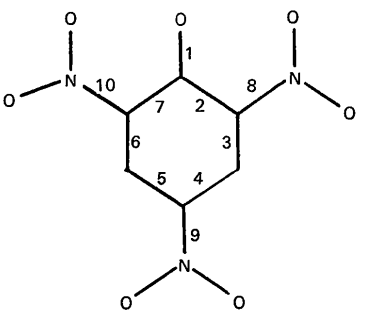
angle in aromatic nitro compounds which was noted by Coppens in 1962. (Using his data one would predict O–N–O angles at approximately 121° at N(37) and 124° at N(34) from the observed bond lengths.)

Tables 6 and 7 contain a summary of some of the bonding data in nitrophenols and nitrophenolates and show the remarkably large change in geometry which occurs on loss of the phenolic proton. Comparison with the present structure shows very plainly that it is anionic and that as such, it is entirely typical.

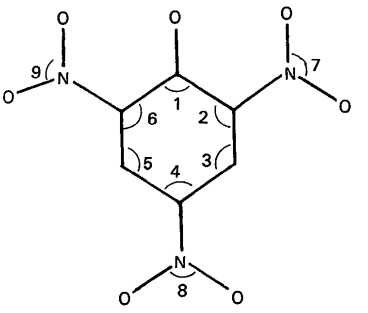
In general dissociation of the phenolic proton results in a 0·1 Å shortening of the C–O bond but a comparison with aldehydes and ketones shows that it is not a pure double bond. The C–C bonds adjacent to the phenolic O atom are lengthened by 0·05 Å to approach the length of a C_{sp2}–C_{sp2} single bond (Haugen & Trætteberg, 1966) and the ring angle at the phenolic site is reduced to 111·8°. The latter reduction is absorbed by a 4° increase in the ring angles at the two *ortho* C atoms so that the remainder of the ring retains a regular hexagonal shape although it is slightly contracted. These data imply a major delocalization of the anionic charge.

Andersen (1971) and Andersen & Andersen (1975*a*) have demonstrated a linear correlation between the strength of an organic hydroxylic acid and the length of the acid C–O bond. This relationship applies to both the acid and its anion. Although the pK_a values of most nitrophenols are available the only crystal structures

Table 6. *Bond lengths* (Å) *and angles* (°) *in nitrophenols*



Bonds



Angles

Compound	1	2	3	4	5	6	7	8	9	10	e.s.d.	Ref
α-*p*-Nitrophenol	1·351	1·393	1·380	1·383	1·388	1·377	1·387		1·422		0·006	*a*
β-*p*-Nitrophenol	1·361	1·396	1·382	1·393	1·394	1·378	1·399		1·450		0·003	*b*
Picric acid π-complex	1·330	1·350	1·350	1·410	1·370	1·390	1·410	1·460	1·440	1·510	0·015	*c*
p-Nitrophenol adduct	1·340	1·410	1·390	1·370	1·370	1·390	1·370		1·470		0·023	*d*
2-Chloro-4,6-dinitrophenol	1·333	1·407	1·370	1·376	1·382	1·370	1·402	1·464	1·472		0·007	*e*
Weighted mean values	1·355	1·396	1·379	1·389	1·391	1·377	1·397	1·463 (6)	1·451		0·002	

Compound	1	2	3	4	5	6	7	8	9	e.s.d.	Ref.
α-*p*-Nitrophenol	122·3	118·9	119·4	120·9	120·1	118·6		122·0		0·4	*a*
β-*p*-Nitrophenol	122·0	118·7	120·0	120·5	120·0	118·8		122·0		0·3	*b*
Picric acid π-complex	119·0	123·5	117·1	123·1	116·3	122·3	124·4	124·4	125·3	1·0	*c*
p-Nitrophenol adduct	120·2	119·3	118·7	123·3	118·2	120·5		123·9		1·5	*d*
2-Chloro-4,6-dinitrophenol	116·7	122·7	117·5	123·0	118·2	122·0	123·4	124·0		0·4	*e*
Weighted mean values	120·6	119·9	119·1	121·4	119·4	119·7	123·5 (3)	122·6		0·2	

References: (*a*) Coppens & Schmidt (1965*a*). (*b*) Coppens & Schmidt (1965*b*). (*c*) Carstensen-Oeser, Göttlicher & Habermehl (1968). (*d*) Baker, Hall & Waters (1970). (*e*) Andersen & Andersen (1975*a*).

containing nitrophenolate anions are those shown in Table 7 and these are mostly picrates. Assuming the linear relationships, the length of the 2BDNP C–O bond suggests a pK_a of approximately 4, similar to that of 2,4-dinitrophenol (3·96). Unfortunately no experimental value has been reported and the recently determined crystal structure of the 2-chloro analogue of 2BDNP (Andersen & Andersen, 1975*a*) (pK_a 2·1) does not contain the phenol in an anionic form.

(*c*) *The* N(9)–O(32) *hydrogen bond*

The distance between the 'bonded' atoms in the two parts of the ERTE-2BDNP molecule, 2·61 (1) Å, is considerably shorter than the normal N···O separation in hydrogen-bonded systems (Pimentel & McLellan, 1960; Jönsson, 1973). The contact is also very much shorter than the sum of the van der Waals radii of N and O [1·52 and 1·55 Å respectively, Bondi (1964)] and must imply a strong hydrogen bond.

The phenolic H atom was not located during the structure determination, but since the geometry of the 2BDNP moiety implies that it is anionic and the lengths of the C–N bonds in the ERTE moiety suggest C–NH^+ bonds, it seems reasonable to assume that the N(9)–O(32) contact is a hydrogen bond of the $NH^+\cdots O^-$ type. This assumption is supported by the pK_a values of 2BDNP (approximately 4, see above) and of protonated erythrina alkaloids [erythraline hydrochloride has a pK_a of 5·97 and is the most acidic of the protonated erythrina alkaloids (Boekelheide, 1960)]. The position of H(9) was therefore calculated assuming a linear hydrogen bond of the $NH^+\cdots O^-$ type and an N–H bond length of 1·06 Å (Jönsson, 1973).

The crystal structure

Owing to the shape of the erythristemine moiety, the packing of the molecules to form the crystal structure is difficult to illustrate without serious overlap. Fig. 5 is a stereoscopic diagram looking along the *b* axis from 'below' the unit cell and shows four asymmetric units related by unit-cell translations in the **a** and **c** directions and two 2BDNP moieties from molecules

Table 7. *Bond lengths* (Å) *and angles* (°) *in nitrophenolates*

Bond numbering as in Table 6.

Compound	1	2	3	4	5	6	7	8	9	10	e.s.d.	Ref.
Potassium *o*-nitrophenolate	1·298	1·421	1·393	1·347	1·383	1·372	1·414	1·433			0·006	*a*
Potassium picrate	1·282	1·467	1·373	1·407	1·407	1·373	1·467	1·472	1·423	1·472	0·009	*b*
	1·243	1·452	1·372	1·382	1·382	1·372	1·452	1·457	1·436	1·457	0·006	*c*
	1·245	1·455	1·370	1·389	1·389	1·370	1·455	1·458	1·440	1·459	0·002	*d*
Ammonium picrate	1·239	1·450	1·372	1·368	1·368	1·372	1·450	1·461	1·457	1·461	0·005	*c*
Potassium *o*-nitrophenolate.$\frac{1}{2}H_2O$	1·260	1·460	1·420	1·400	1·290	1·380	1·430	1·390			0·040	*e*
	1·281	1·425	1·407	1·375	1·397	1·360	1·440	1·422			0·006	*f*
Diazepin picrate	1·245	1·436	1·402	1·379	1·384	1·356	1·485	1·458	1·442	1·458	0·008	*g*
Serotonin picrate.H_2O	1·240	1·457	1·375	1·378	1·389	1·366	1·451	1·438	1·449	1·459	0·004	*h*
Tryptamine picrate	1·248	1·448	1·371	1·374	1·385	1·362	1·450	1·450	1·447	1·449	0·004	*i*
D,L-Tryptamine picrate.MeOH	1·251	1·443	1·368	1·374	1·370	1·374	1·448	1·457	1·451	1·442	0·004	*i*
Guanine picrate.H_2O	1·238	1·459	1·373	1·380	1·381	1·374	1·460	1·449	1·446	1·449	0·004	*j*
6-Thioguanine picrate	1·239	1·459	1·363	1·370	1·374	1·388	1·462	1·454	1·454	1·452	0·007	*j*
Succinylcholine picrate	1·234	1·480	1·357	1·382	1·398	1·374	1·448	1·455	1·438	1·470	0·007	*k*
Lead picrate complex	1·220	1·460	1·330	1·330	1·370	1·370	1·420	1·560	1·440	1·480	0·040	*l*
ERTE-2BDNP	1·270	1·430	1·360	1·360	1·360	1·380	1·440	1·430	1·470		0·010	*m*
Weighted mean values	1·248	1·451	1·373	1·380	1·384	1·370	1·444	1·452	1·445	1·443	0·001	

Compound	1	2	3	4	5	6	7	8	9	e.s.d.	Ref.
Potassium *o*-nitrophenolate	114·7	121·7	121·2	119·3	120·9	122·3		119·8		0·5	*a*
Potassium picrate	111·1	124·9	118·5	122·0	118·5	124·9	122·6	123·3	122·6	0·5	*c*
Ammonium picrate	111·5	124·2	119·1	121·9	119·1	124·2	123·3	124·0	122·3	0·3	*c*
Potassium *o*-nitrophenolate.$\frac{1}{2}H_2O$	113·0	122·0	118·0	122·0	122·1	123·0		122·0		3·0	*e*
	115·2	122·5	119·5	119·6	121·8	121·5		118·7		0·5	*f*
Diazepin picrate	111·8	123·1	119·8	120·7	120·1	123·4	122·4	124·4	124·8	0·9	*g*
Serotonin picrate.H_2O	111·1	123·9	119·9	120·8	118·8	125·3	120·3	123·3	122·4	0·3	*h*
Tryptamine picrate	111·8	123·8	119·7	121·1	119·1	124·5	121·3	122·5	122·0	0·3	*i*
D,L-Tryptamine picrate.MeOH	112·1	124·0	119·4	121·4	119·5	123·6	121·7	123·7	120·1	0·3	*i*
Guanine picrate.H_2O	111·6	124·0	119·5	121·4	119·4	124·1	121·0	123·1	121·2	0·2	*j*
6-Thioguanine picrate	111·6	123·6	120·3	122·0	118·4	124·1	122·2	123·1	121·4	0·4	*j*
Succinylcholine picrate	110·4	124·4	119·7	121·3	118·1	125·8	123·1	123·3	123·5	0·5	*k*
Lead picrate complex	109·0	128·0	119·0	119·0	122·0	122·0	120·8	121·0		2·0	*l*
ERTE-2BDNP	113·0	123·3	120·4	122·7	117·1	124·4	122·0	124·3	120·0	1·1	*m*
Weighted mean values	111·8	123·8	119·6	121·2	119·3	124·1	121·6	122·6	120·7	0·1	

References: (*a*) Bush & Truter (1971). (*b*) Bettman & Hughes (1954). (*c*) Maartman-Moe (1969). (*d*) Palenik (1972). (*e*) Richards (1961). (*f*) Andersen & Andersen (1975*b*). (*g*) Gerdil (1972). (*h*) Thewalt & Bugg (1972). (*i*) Gartland, Freeman & Bugg (1974). (*j*) Bugg & Thewalt (1975). (*k*) Jensen (1975). (*l*) Herbstein & Kaftory (1972). (*m*) This paper.

generated by the diad screw axes. It shows the most characteristic feature of the crystal packing, namely the alternating parallel arrangement of the ERTE (ring *D*) and the 2BDNP molecules to form continuous stacks or columns. Fig. 6 shows the arrangement of molecules within these columns. The ERTE cations marked '1' and '3' in the figure are related by a unit-cell translation in the **a** direction and '2' is an intruding anion from a symmetry-related molecule. The pattern shown in Fig. 6 is repeated continuously to form the columns. The figure shows that the aromatic moieties are stacked obliquely to the column axis, a feature which is very common in crystals of aromatic compounds.

Fig. 6 also contains the lengths of the shorter intramolecular contacts within the columns, and shows that these fall into two categories. The contacts in the first category are normal van der Waals contacts between sp^3-hybridized atoms in molecule 1 and sp^2-hybridized atoms in molecule 2. The contacts in the second category are between atoms in molecules 2 and 3 which are all sp^2-hybridized and may imply π–π interaction.

Ring *D*, the aromatic ring in the ERTE moiety, carries two methoxy and two aliphatic substituent groups. Since methoxy groups are strongly and aliphatic groups weakly electron donating, the aromatic ring should be comparatively rich in electrons and thus able to donate charge to the strongly electron accepting 2BDNP group to form a π-molecular complex. Compounds of this type have been reviewed by Prout & Wright (1968) and very extensively by Herbstein (1971). In general the donor–acceptor process results in a coloured compound owing to the formation of a charge-transfer band in the visible region of the spectrum (*ca* 460 nm for nitro-aromatic acceptors). Crystals of the present compound were an intense yellow whereas erythristemine itself is white.

The contact distances between molecules 2 and 3 in Fig. 6 are typical C–N and C–O intermolecular distances for π–π compounds with nitro-aromatic acceptors. The presence of the 11-methoxy group in the ERTE molecule and the C(7)–O(18) and C(19) intermolecular contacts prevent the close approach of ring *D* in molecule 1 to the 2BDNP molecule (2) so that the π–π interaction is not continuous through the columns of molecules.

The van der Waals volume of the ERTE-2BDNP molecule, calculated using the increments tabulated by Bondi (1968), is 465 Å^3 giving a packing coefficient (Kitaigorodsky, 1957) of 0·689. This is a typical value for simple aromatic compounds and probably reflects the parallel packing of the aromatic moieties in the structure.

The work which is described in this paper was carried out in the Chemical Crystallography Laboratory, Imperial College, London, under the supervision of Professor D. Rogers with the aid of equipment

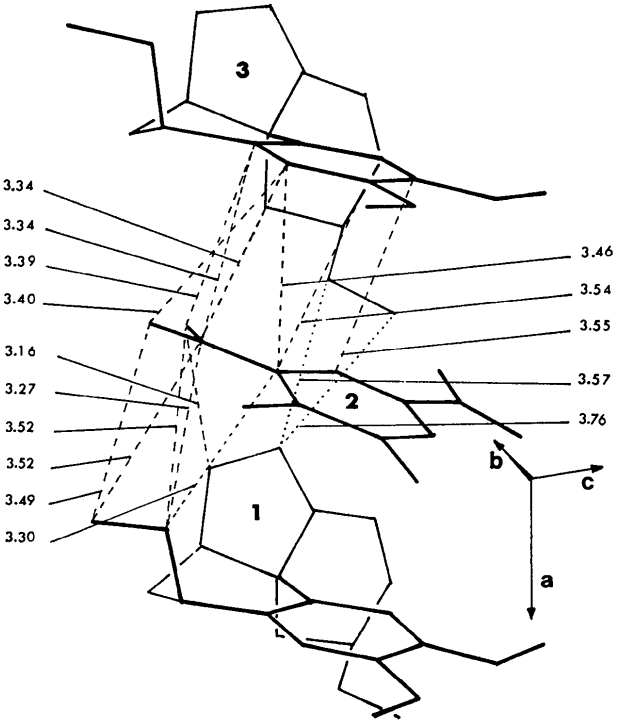


Fig. 6. Intramolecular contacts.

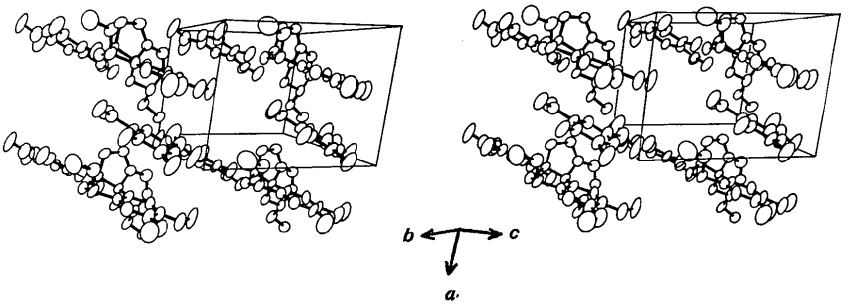


Fig. 5. The crystal structure.

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