C(15)—C(16)	1.355 (11)	C(215)—C(216)	1.352 (11)
C(16)—C(17)	1.323 (11)	C(216)—C(217)	1.362 (10)
C(17)—C(18)	1.402 (13)	C(217)—C(218)	1.383 (8)
C(4a)—C(5)—Br(1)	118.9 (6)	C(24a)—C(25)—Br(2)	118.3 (5)
C(5a)—C(5)—Br(1)	118.8 (4)	C(25a)—C(25)—Br(2)	119.2 (6)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*R*,*S*)-1-Phenylethylammonium (*S*)-Mandelate

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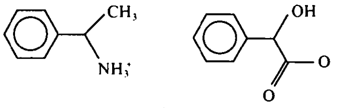
Abstract

The asymmetric unit of the title compound, $C_8H_{12}N^+.C_8H_7O_3^-$, contains two 1-phenylethylammonium cations with opposite configurations and two (*S*)-mandelate anions (α-hydroxybenzeneacetate). The ions are shown to be nearly related by a pseudo inversion centre. This gives rise to an unusual conformation of one of the (*S*)-mandelate ions. An extensive hydrogen-bond system connects the ions in a similar way to the hydrogen-bond patterns found in (*S*)-1-phenylethylammonium (*S*)-mandelate and (*R*)-mandelate.

Comment

The title compound has been isolated as part of an investigation into salts formed between 1-phenylethylamine and mandelic acid. When racemic 1-phenylethylamine and (*S*)-mandelic acid are mixed in equimolar amounts, (*S*)-1-phenylethylammonium (*S*)-mandelate precipitates as the less soluble salt (Larsen & Lopez de Diego, 1993; Brianso, Leclercq & Jacques, 1979). After filtration of the solution, (*R*,*S*)-1-phenylethylammonium (*S*)-mandelate, (I), precipitates from the mother liquor. The crystal structure of this salt is described below and its pseudo-inversion symmetry is discussed.



(I)

The four ions in the asymmetric unit are shown in Fig. 1. In the numbering of the atoms, O1 is selected as the carboxylate O atom with the smaller torsion angle O1—C1—C2—O3 to the hydroxy atom O3, and the phenyl ring is numbered with C4 in the *anti* position with respect to the OH group. In the 1-phenylethylammonium ion, C12 is *anti* to the amine group.

The conformation of the 1-phenylethylammonium ion is determined by the torsion angle N—C10—C11—C12, given in Table 2. If the torsion angles of two enantiomers have the same numerical values but opposite signs, they adopt the same conformation. As seen from Table 2, the conformation of the two cations differs only by 10°. A similar conformation is found in the less soluble salt (*S*)-1-phenylethylammonium (*S*)-mandelate, where N—C10—C11—C12 = 144.2 (2)°. In an investigation of the structural features of mandelate compounds, the torsion angle O1—C1—C2—O3 for all (*S*)-mandelate ions was found to be within the range −40 to +10°, with most values between −20 and +10° (Larsen & Lopez de Diego, 1993). In the present structure, the (*S*)-mandelate ion labelled *A* has this torsion angle within the most common range while the ion labelled *B* adopts an unusual conformation with O1—C1—C2—O3 = −56.8 (2)°. The atom numbering is related to the position of O3. Inspection of the torsion angles in the mandelate ions, given in Table 2, shows that opposite numbering of the carboxylic O atoms and the C atoms in the phenyl ring of the *B* anion would give torsion angles similar to those in the *A* anion, but with opposite signs. This would have been the numbering if O3*B* and H2*B* (attached to C2*B*) were interchanged, thus giving a common conformation of the resulting (*R*)-

mandelate ion. It can be seen from Fig. 1 that if O3*B* and H2*B* are interchanged, the anions are close to being mirror images of each other.

Inspection of the stereodrawing, Fig. 2, shows that the structure displays a pseudo inversion centre of symmetry. If the atomic coordinates of all atoms in the *A* ions are transformed by the relation $(-x+1.5, -y+2, -z+1)$, the resulting coordinates are very similar to those of the corresponding atoms in the ions if the atomic numbering in the *B* anion is changed as described above. The average deviation from this inversion symmetry is 0.060 (4) Å with a maximum value of 0.148 (4) Å, if O3 is excluded.

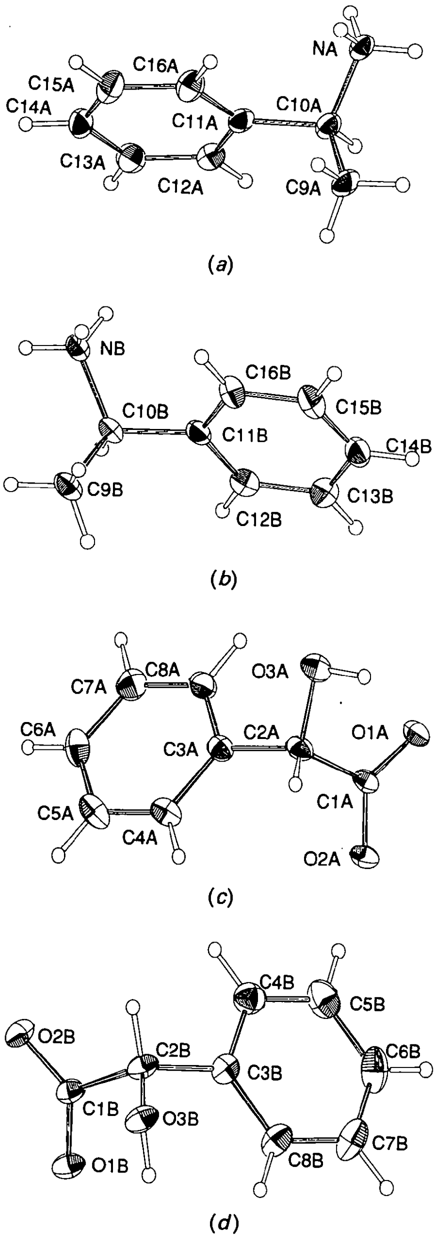


Fig. 1. *ORTEP*II (Johnson, 1971) drawings of (*a*) the (*S*)-1-phenylethylammonium ion, (*b*) the (*R*)-1-phenylethylammonium ion, and (*c*) and (*d*) the (*S*)-mandelate ions, illustrating the atomic numbering scheme. The displacement ellipsoids enclose 50% probability and the H atoms are drawn as spheres of fixed radii.

The hydrogen-bond geometry is given in Table 3. Two hydrogen bonds are found between the ammonium group in each cation labelled *A* and the carboxylate group of each of two *A* anions, forming chains in the direction of the crystallographic *b* axis. The *B* cations and *B* anions also form chains in the same direction. These *A* and *B* chains are linked by hydrogen bonds from ammonium groups to carboxylate groups on one side and between hydroxy groups on the other side, extending the hydrogen-bonding pattern into sheets parallel to the *bc* plane. The hydrogen bonds are drawn as thin lines in the stereo packing diagram (Fig. 2). Very similar hydrogen-bond patterns are found in the less soluble salt (*S*)-1-phenylethylammonium (*S*)-mandelate (Larsen & Lopez de Diego, 1993) and in the more soluble salt (*R*)-1-phenylethylammonium (*S*)-mandelate (Lopez de Diego, 1994).

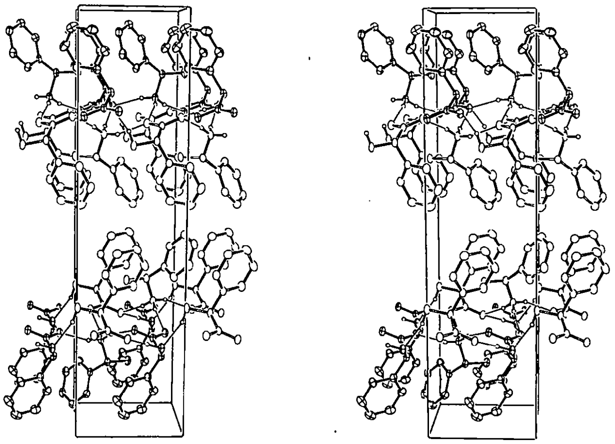


Fig. 2. Stereoview of the packing in (*R*,*S*)-1-phenylethylammonium (*S*)-mandelate seen in the direction of the crystallographic *c* axis with *a* axis vertical and *b* horizontal. The ions labelled *A* are identified by plain ellipsoids and open bonds, and those labelled *B* by ellipsoids with principal ellipses and filled bonds. The hydrogen bonds are drawn as thin lines.

Experimental

Crystal data

$C_8H_{12}N^+.C_8H_7O_3^-$
$M_r = 273.33$
Monoclinic
$P2_1$
$a = 25.543$ (4) Å
$b = 6.5659$ (8) Å
$c = 8.6913$ (12) Å
$\beta = 93.663$ (11)°
$V = 1454.7$ (3) Å^3
$Z = 4$
$D_x = 1.248$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 27.98$–43.29°
$\mu = 0.697$ mm^{-1}
$T = 122.0$ (5) K
Prismatic
0.40 × 0.13 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
7668 measured reflections
5985 independent reflections
5789 observed reflections [$|F_o| > 4\sigma(|F_o|)$]

$R_{\rm int} = 0.0219$
$\theta_{\rm max} = 75.12°$
$h = -32 \rightarrow 31$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 166 min
intensity variation: 7%

Refinement

Refinement on F^2
$R(F) = 0.0511$
$wR(F^2) = 0.1487$
$S = 1.059$
5982 reflections
371 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1126P)^2 + 0.2248P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.316$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.356$ e Å^{-3}
Atomic scattering factors from *SHELXL*93 (Sheldrick, 1993)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
C1A	0.7277 (1)	0.7771 (3)	0.2076 (2)	0.019 (1)
O1A	0.7318 (1)	0.6508 (2)	0.3163 (2)	0.024 (1)
O2A	0.7471 (1)	0.9535 (2)	0.2134 (1)	0.023 (1)
C2A	0.6958 (1)	0.7194 (3)	0.0581 (2)	0.021 (1)
O3A	0.6853 (1)	0.5067 (2)	0.0482 (2)	0.030 (1)
C3A	0.6441 (1)	0.8321 (3)	0.0560 (2)	0.021 (1)
C4A	0.6372 (1)	1.0164 (3)	−0.0222 (2)	0.027 (1)
C5A	0.5895 (1)	1.1189 (4)	−0.0207 (2)	0.034 (1)
C6A	0.5489 (1)	1.0401 (4)	0.0591 (2)	0.032 (1)
C7A	0.5560 (1)	0.8574 (4)	0.1393 (2)	0.030 (1)
C8A	0.6033 (1)	0.7548 (3)	0.1369 (2)	0.026 (1)
C9A	0.6486 (1)	0.9862 (3)	0.4973 (2)	0.026 (1)
C10A	0.6491 (1)	1.1887 (3)	0.4103 (2)	0.022 (1)
NA	0.7047 (1)	1.2559 (2)	0.3980 (2)	0.021 (1)
C11A	0.6176 (1)	1.3480 (3)	0.4901 (2)	0.022 (1)
C12A	0.5687 (1)	1.4045 (3)	0.4236 (2)	0.025 (1)
C13A	0.5369 (1)	1.5392 (4)	0.4989 (2)	0.029 (1)
C14A	0.5540 (1)	1.6176 (3)	0.6408 (2)	0.028 (1)
C15A	0.6026 (1)	1.5634 (3)	0.7074 (2)	0.030 (1)
C16A	0.6342 (1)	1.4272 (3)	0.6331 (2)	0.027 (1)
C1B	0.7730 (1)	1.2250 (3)	0.7819 (2)	0.020 (1)
O1B	0.7540 (1)	1.0494 (2)	0.7847 (2)	0.024 (1)
O2B	0.7680 (1)	1.3485 (2)	0.6709 (1)	0.024 (1)
C2B	0.8070 (1)	1.2931 (3)	0.9261 (2)	0.021 (1)
O3B	0.7787 (1)	1.2795 (2)	1.0610 (1)	0.024 (1)
C3B	0.8575 (1)	1.1700 (3)	0.9349 (2)	0.022 (1)
C4B	0.8990 (1)	1.2340 (4)	0.8501 (2)	0.030 (1)
C5B	0.9453 (1)	1.1227 (4)	0.8518 (2)	0.035 (1)
C6B	0.9510 (1)	0.9481 (4)	0.9402 (2)	0.038 (1)
C7B	0.9103 (1)	0.8834 (4)	1.0241 (2)	0.037 (1)
C8B	0.8632 (1)	0.9911 (4)	1.0209 (2)	0.028 (1)
C9B	0.8495 (1)	1.0092 (3)	0.4964 (2)	0.026 (1)
C10B	0.8464 (1)	0.8091 (3)	0.5828 (2)	0.021 (1)
NB	0.7901 (1)	0.7470 (2)	0.5896 (2)	0.021 (1)
C11B	0.8785 (1)	0.6474 (3)	0.5069 (2)	0.021 (1)
C12B	0.9296 (1)	0.6120 (3)	0.5651 (2)	0.027 (1)
C13B	0.9620 (1)	0.4801 (4)	0.4904 (2)	0.031 (1)
C14B	0.9434 (1)	0.3817 (3)	0.3571 (2)	0.029 (1)
C15B	0.8924 (1)	0.4152 (3)	0.2989 (2)	0.029 (1)
C16B	0.8600 (1)	0.5474 (3)	0.3736 (2)	0.026 (1)

Table 2. *Selected geometric parameters* (Å, °)

O1A—C1A	1.257 (2)	O1B—C1B	1.252 (2)
O2A—C1A	1.260 (2)	O2B—C1B	1.260 (2)
C1A—C2A	1.536 (2)	C1B—C2B	1.544 (2)
C2A—O3A	1.423 (2)	C2B—O3B	1.420 (2)
C2A—C3A	1.514 (2)	C2B—C3B	1.520 (3)
C3A—C4A	1.394 (3)	C3B—C4B	1.393 (3)
C3A—C8A	1.389 (3)	C3B—C8B	1.395 (3)
C4A—C5A	1.392 (3)	C4B—C5B	1.390 (3)
C5A—C6A	1.384 (3)	C5B—C6B	1.383 (4)
C6A—C7A	1.393 (3)	C6B—C7B	1.375 (3)
C7A—C8A	1.385 (3)	C7B—C8B	1.394 (3)
NA—C10A	1.498 (2)	NB—C10B	1.500 (2)
C9A—C10A	1.530 (3)	C9B—C10B	1.517 (3)
C10A—C11A	1.514 (3)	C10B—C11B	1.517 (2)
C11A—C12A	1.393 (3)	C11B—C12B	1.390 (3)
C11A—C16A	1.388 (3)	C11B—C16B	1.388 (2)
C12A—C13A	1.392 (3)	C12B—C13B	1.388 (3)
C13A—C14A	1.381 (3)	C13B—C14B	1.384 (3)
C14A—C15A	1.382 (3)	C14B—C15B	1.384 (3)
C15A—C16A	1.391 (3)	C15B—C16B	1.388 (3)
O1A—C1A—O2A	124.3 (2)	C5B—C6B—C7B	119.6 (2)
O1A—C1A—C2A	119.2 (2)	C6B—C7B—C8B	120.9 (2)
O2A—C1A—C2A	116.6 (2)	C3B—C8B—C7B	119.9 (2)
C1A—C2A—O3A	112.4 (2)	NA—C10A—C9A	109.2 (2)
C1A—C2A—C3A	107.74 (14)	NA—C10A—C11A	111.2 (2)
O3A—C2A—C3A	108.5 (2)	C9A—C10A—C11A	110.68 (14)
C2A—C3A—C4A	120.9 (2)	C10A—C11A—C12A	118.8 (2)
C2A—C3A—C8A	119.8 (2)	C10A—C11A—C16A	121.9 (2)
C4A—C3A—C8A	119.3 (2)	C12A—C11A—C16A	119.1 (2)
C3A—C4A—C5A	119.9 (2)	C11A—C12A—C13A	120.6 (2)
C4A—C5A—C6A	120.5 (2)	C12A—C13A—C14A	119.8 (2)
C5A—C6A—C7A	119.7 (2)	C13A—C14A—C15A	120.1 (2)
C6A—C7A—C8A	119.8 (2)	C14A—C15A—C16A	120.2 (2)
C3A—C8A—C7A	120.8 (2)	C11A—C16A—C15A	120.2 (2)
O1B—C1B—O2B	125.9 (2)	NB—C10B—C9B	109.62 (14)
O1B—C1B—C2B	116.7 (2)	NB—C10B—C11B	111.85 (14)
O2B—C1B—C2B	117.4 (2)	C9B—C10B—C11B	110.10 (14)
C1B—C2B—O3B	111.22 (14)	C10B—C11B—C12B	118.7 (2)
C1B—C2B—C3B	108.59 (14)	C10B—C11B—C16B	122.0 (2)
O3B—C2B—C3B	113.6 (2)	C12B—C11B—C16B	119.0 (2)
C2B—C3B—C4B	119.0 (2)	C11B—C12B—C13B	120.6 (2)
C2B—C3B—C8B	122.3 (2)	C12B—C13B—C14B	119.9 (2)
C4B—C3B—C8B	118.7 (2)	C13B—C14B—C15B	119.8 (2)
C3B—C4B—C5B	120.8 (2)	C14B—C15B—C16B	120.2 (2)
C4B—C5B—C6B	120.1 (2)	C11B—C16B—C15B	120.4 (2)
O1A—C1A—C2A—O3A	−14.6 (2)		
O1A—C1A—C2A—C3A	104.9 (2)		
O2A—C1A—C2A—C3A	−73.4 (2)		
C1A—C2A—C3A—C4A	96.0 (2)		
C1A—C2A—C3A—C8A	−81.9 (2)		
NA—C10A—C11A—C12A	132.0 (2)		
O1B—C1B—C2B—O3B	−56.8 (2)		
O1B—C1B—C2B—C3B	68.9 (2)		
O2B—C1B—C2B—C3B	−109.4 (2)		
C1B—C2B—C3B—C4B	83.8 (2)		
C1B—C2B—C3B—C8B	−93.9 (2)		
NB—C10B—C11B—C12B	−142.1 (2)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*···*A*	H···*A*	*D*—H···*A*
NA—HN1A···O2A	2.813 (2)	1.912 (2)	170.5 (6)
NA—HN2A···O1A$^{\rm i}$	2.787 (2)	1.940 (5)	154.0 (9)
NA—HN3A···O2B	2.849 (2)	1.965 (3)	163.5 (7)
NB—HN1B···O1B	2.805 (2)	1.914 (3)	165.6 (7)
NB—HN2B···O2B$^{\rm ii}$	2.778 (2)	1.907 (5)	159.7 (11)
NB—HN3B···O1A	2.794 (2)	1.917 (4)	161.4 (9)
O3A—HO3A···O3B$^{\rm iii}$	2.809 (2)	1.97 (3)	162 (3)
O3B—HO3B···O2A$^{\rm iv}$	2.669 (2)	1.84 (3)	148 (2)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, y - 1, z$; (iii) $x, y - 1, z - 1$; (iv) $x, y, 1 + z$.

Data reduction, including corrections for intensity variation, was performed with the *DREADD* programs (Blessing, 1987). The structure was solved by direct methods using *SHELXS*86

(Sheldrick, 1990). *SHELXL93* (Sheldrick, 1993) was used to refine the structure. Anisotropic displacement parameters were used for all non-H atoms. H atoms bonded to tertiary and aromatic C atoms were fixed in calculated positions, the H atoms in the hydroxy groups were located from a $\Delta\rho$ map and the remaining H atoms were refined with the restraint of a fixed angle and distance to the non-H atoms. The absolute configuration was chosen so as to be in agreement with the known absolute configuration of (*S*)-mandelic acid, the choice being supported by a Flack (1983) parameter of $\chi = -0.35\,(17)$. Although the compound contains both enantiomers of the 1-phenylethylammonium ion, it contains only the *S* form of the mandelate ion. Consequently the salt cannot crystallize in a centrosymmetric space group.

I am grateful to Mr Flemming Hansen for help with the experimental crystallographic work and Dr Sine Larsen for valuable discussions. Support from The Carlsberg Foundation is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AB1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 1998–2000

Structures of Pyrazolo[1,5-*a*]pyridine Derivatives

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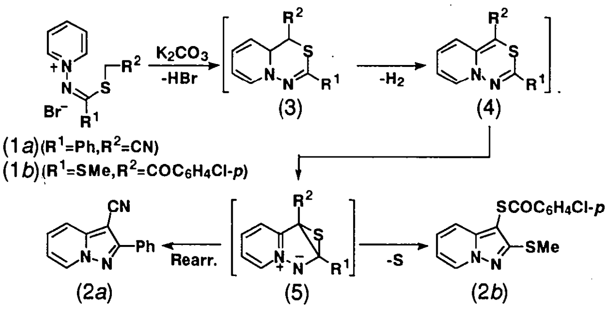
Abstract

The pyrazolo[1,5-*a*]pyridine skeletons of 2-phenylpyrazolo[1,5-*a*]pyridine-3-carbonitrile, $C_{14}H_9N_3$ (2*a*), and *S*-2-methylthiopyrazolo[1,5-*a*]pyridin-3-yl *p*-chlorothiobenzoate, $C_{15}H_{11}ClN_2OS_2$ (2*b*), are planar [maximum deviation 0.019 (3) Å for (2*a*) and 0.011 (5) Å for (2*b*)]. The pyrazolo[1,5-*a*]pyridine skeleton of compound (2*b*), in which the 2- and 3-substituents are bonded to the pyrazole ring by two long C—S bonds, shows no significant distortion, while in (2*a*), with the 2-phenyl and the 3-cyano groups, considerable changes are seen in the bond angles resulting from the severe steric interaction accompanied by the resonance effect between the pyrazolo[1,5-*a*]pyridine and the phenyl group.

Comment

The present study was undertaken to confirm the chemical structures of the title compounds, (2*a*) and (2*b*), and to determine their geometrical characteristics, which are undiscernible from their formation paths. Structural data for pyrazolo[1,5-*a*]pyridine derivatives are scarce.



The pyrazolo[1,5-*a*]pyridine rings in these molecules are almost planar [maximum deviation 0.019 (3) Å for (2*a*) and 0.011 (5) Å for (2*b*)] and constitute bicyclic 10π-electron aromatic systems. The bond distances and angles for (2*b*) are very similar to those of the INDO-optimized geometry for the parent pyrazolo[1,5-*a*]pyridine (Catalan *et al.*, 1988), except for the N(1)—N(2) bond length (1.3253 Å in the latter) and the N(1)—N(2)—C(1) angle (104.1° in the latter). Furthermore, the angle S(1)—C(1)—N(2) in (2*b*) is very similar to the angle S(1)—C(1)—C(2), and the angle S(2)—C(2)—C(1) is also very similar to the angle S(2)—C(2)—C(3), indicating the absence of any steric interaction between their substituents. The absence of such interaction must be caused by the two long C(1)—S(1) and C(2)—S(2) bonds. On the other hand, the geometry of the pyrazole moiety of (2*a*) is somewhat different from that of (2*b*). Owing to the extension of the conjugated system between the 2-phenyl group and the pyrazolo[1,5-*a*]pyridine ring [the dihedral angle is 6.3 (2)°] in (2*a*), a severe repulsion between the 2-phenyl and the 3-cyano groups is induced, as seen in the increase of the three bond angles C(2)—C(1)—C(8), C(1)—C(2)—C(14) and C(1)—C(8)—C(13), and in the deviation of the 2-cyano group from the plane of the ring.