

A Charge-Transfer Complex: Bis(2,4,6-trimethyl-1-pyridyl)iodonium Perchlorate

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Abstract. $(C_8H_{11}N)_2I^+ \cdot ClO_4^-$, $M_r = 468.72$, monoclinic, $C2/c$, $a = 27.844$ (5), $b = 11.036$ (2), $c = 23.412$ (7) Å, $\beta = 126.47$ (2)°, $V = 5785.7$ Å³, $Z = 12$, $d_o = 1.60$, $d_c = 1.61$ Mg m⁻³, $R = 0.057$ and $R_w = 0.065$ for 2171 reflections [$I > 2\sigma(I)$]. Bis(2,4,6-trimethyl-1-pyridyl)iodonium perchlorate crystallized with 1.5 formula weights per asymmetric unit; two conformations of the bis(2,4,6-trimethyl-1-pyridyl)iodonium cation are observed. The cation in the general position has a propeller-like twist conformation of the two γ -collidine (synonymous with 2,4,6-trimethyl-1-pyridyl) planes (dihedral angle 35.7°) whereas the cation with the iodine on the centre of symmetry has the two γ -collidine rings parallel but the planes are separated by 1.34 Å. The three unique I–N charge-transfer bond lengths average 2.29 (1) Å.

Introduction. The geometry of charge-transfer complexes of tertiary amines with dihalogens is well established (Strømme, 1959; Hassel & Hope, 1960; Hassel & Rømming, 1967). The N–X–X ($X =$ halogen) bond pattern is linear with N–I distances of 2.26–2.31 Å. These lengths are longer than expected for the sum of the covalent radii (2.03 Å) but much shorter than the sum of the van der Waals radii of I and N (~3.55 Å; Bondi, 1964). It has been noted that charge-transfer complexes involving two heteroaromatic amines and I^+ should have many of the properties of the previously mentioned dihalogen-amine complexes (Hassel, 1970). This inference was made from the results of the determination of the structure of pyridine. $2I_2$ (Hassel & Hope, 1961) which contains dipyridyliodonium ions.

The preparation of bis(2,4,6-trimethyl-1-pyridyl)iodonium perchlorate (the 2,4,6-trimethylpyridyl group is also referred to as γ -collidine below) and the isomorphous bis(γ -collidine)bromonium perchlorate has been described by Lemieux & Morgan (1965). It was of interest to determine the effect that the two *ortho* methyl groups might have on the geometry of these charge-transfer complexes. The I–N distance in the structure of pyridine. $2I_2$ is 2.16 Å (Hassel & Hope, 1961).

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Well formed, multifaceted, transparent, colorless single crystals of both bis(2,4,6-trimethyl-1-pyridyl)iodonium perchlorate and the corresponding bromonium salt were obtained by slow diffusion of petroleum ether into a methylene dichloride solution of each compound. Preliminary diffraction photographs established that the space group is $C2/c$ or Cc and that the crystals of the bromonium complex [$a = 27.275$ (9), $b = 11.043$ (2), $c = 23.548$ (8) Å and $\beta = 127.2$ (1)°, measured on an FACS-1 diffractometer] were isomorphous with those of the iodonium complex.

X-ray intensities for crystals of bis(γ -collidine)iodonium perchlorate were measured at 291 K on a Picker FACS-1 diffractometer (modified with an extended 650 mm crystal-counter diffracted-beam helium path). An approximately equidimensional (0.3 mm) crystal and Ni-filtered Cu $K\alpha$ radiation were used. The intensities were recorded by θ – 2θ scans (1° min⁻¹) and two 10 s fixed-position background counts for all reflections in one quadrant up to $2\theta = 100^\circ$. A correction for linear decay was made from the decrease of the intensities of three monitor reflections with time (maximum 7.7% from initial). The absorption-profile correction was after that of North, Phillips & Mathews (1968). After equivalent $hk0$ and $\bar{h}k0$ reflections were averaged, the calculation of the standard deviation of the intensities (as defined by Stout & Jensen, 1968) indicated that of the 2427 measured, 2171 had $I > 2\sigma(I)$.

The structure was solved by Patterson and Fourier syntheses and refined by full-matrix least squares (unit weights). Anisotropic temperature factors were refined for non-hydrogen atoms. One of the perchlorate ions lies on a twofold axis and exhibits spatial disorder. Hydrogen atoms on the γ -collidine rings were readily located, but those of the methyl groups showed varying degrees of disorder. All H atoms were included in the structure factor calculations ($B = 5.0$ Å²), but none were refined. During the course of refinement attempts to describe the disordered perchlorate ion were not completely successful; a second set of O-atom positions (occupancy $\frac{1}{3}$, estimated from peak heights on the difference map) were determined. Refinement was concluded with a final conventional R value ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) for observed reflections of 0.057; the

Table 1. Positional parameters ($\times 10^4$) and B_{eq} values for non-hydrogen atoms

The equivalent B factors (B_{eq}) are given in \AA^2 .

	x	y	z	B_{eq}
I(1)	2065 (1)	536 (1)	3570 (1)	3.84 (6)
I(2)*	5000	0	5000	3.23 (5)
Cl(1)	1536 (2)	1511 (4)	651 (2)	4.00 (14)
Cl(2)*	5000	998 (7)	7500	8.23 (18)
N(1)	2804 (6)	1780 (12)	4426 (6)	4.3 (6)
N(2)	1295 (5)	-702 (11)	2731 (6)	3.8 (6)
N(3)	4232 (5)	1194 (10)	4136 (5)	3.4 (5)
C(1)	2690 (7)	2966 (16)	4411 (8)	4.2 (7)
C(2)	3136 (7)	3714 (14)	4960 (8)	4.2 (8)
C(3)	3665 (7)	3244 (17)	5520 (8)	4.6 (8)
C(4)	3754 (7)	2020 (16)	5508 (8)	5.0 (8)
C(5)	3320 (7)	1256 (16)	4973 (8)	5.1 (8)
C(6)	2125 (8)	3550 (15)	3798 (8)	5.6 (8)
C(7)	3415 (8)	-95 (15)	4964 (10)	7.5 (9)
C(8)	4152 (8)	4041 (17)	6110 (9)	6.7 (9)
C(9)	871 (7)	-274 (14)	2050 (7)	3.8 (7)
C(10)	378 (7)	-973 (17)	1584 (8)	4.7 (8)
C(11)	295 (7)	-2072 (17)	1761 (8)	4.3 (8)
C(12)	717 (7)	-2508 (14)	2447 (8)	5.3 (7)
C(13)	1226 (7)	-1809 (15)	2926 (8)	4.2 (7)
C(14)	1688 (8)	-2300 (16)	3669 (8)	5.9 (8)
C(15)	981 (8)	935 (16)	1863 (8)	5.7 (8)
C(16)	-253 (7)	-2853 (16)	1256 (8)	5.5 (8)
C(17)	3821 (7)	709 (13)	3479 (7)	3.7 (7)
C(18)	3320 (6)	1369 (14)	3001 (7)	3.9 (7)
C(19)	3223 (6)	2500 (15)	3152 (7)	4.1 (7)
C(20)	3655 (7)	3019 (14)	3809 (8)	3.8 (7)
C(21)	4177 (6)	2333 (14)	4302 (7)	3.8 (7)
C(22)	4662 (8)	2877 (14)	5004 (7)	4.3 (7)
C(23)	2675 (7)	3242 (16)	2632 (8)	5.4 (8)
C(24)	3936 (7)	-514 (14)	3308 (7)	4.8 (7)
O(1)	1007 (5)	770 (11)	265 (6)	6.6 (6)
O(2)	1738 (6)	1738 (11)	228 (7)	7.0 (6)
O(3)	1988 (5)	862 (11)	1265 (6)	7.7 (7)
O(4)	1405 (7)	2620 (12)	816 (7)	8.5 (7)
O(5)*	4860 (17)	1663 (34)	7852 (18)	13.7 (10)
O(6)*	4435 (10)	278 (20)	7010 (11)	8.4 (6)
O(7)*	4880 (20)	350 (40)	6910 (20)	9.0 (-)
O(8)*	5635 (40)	1928 (90)	7417 (50)	20.0 (-)

* The occupancies of I(2) and Cl(2) were 0.5; those for O(5) and O(6) were 0.67 and those for O(7) and O(8), 0.33. The partial occupancies of these several atoms were not refined.

weighted R_w ($= [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$) is 0.065.

The atomic scattering factors for C, N, O, I and Cl were those of Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). The real part of the anomalous dispersion of I and Cl were corrected by values from Cromer & Liberman (1970). The refined atomic parameters are listed in Table 1.* All com-

* Lists of structure factors, anisotropic thermal parameters and hydrogen positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36332 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

putations were done with the XRAY70 system (Stewart, Kundell & Baldwin, 1970).

Discussion. Fig. 1 shows the conformational differences between the two iodonium cations present in the asymmetric unit. The cation occupying a general position has a significant twist with a dihedral angle of 35.7° between the γ -collidine ring planes. The cation that has the iodine on the centre of symmetry has γ -collidine rings that are parallel with planes 1.35 \AA apart. The iodine atoms, I(1) and I(2), are significantly out of the planes of all of the aromatic ring systems.

The atom numbering, bond lengths and interbond angles are contained in Fig. 2. Even though the two cations display such different conformations, the three unique I-N distances are similar and have an average value of 2.29 \AA . The corresponding distance in pyridine. $2I_2$ is 2.16 \AA (Hassel & Hope, 1961) and for

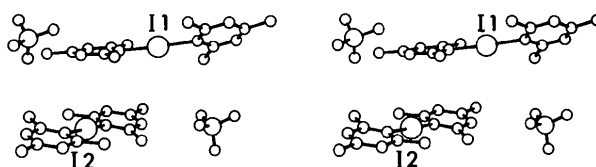


Fig. 1. Stereoscopic drawing of two bis(2,4,6-trimethyl-1-pyridyl)iodonium cations illustrating the conformational differences between the general-position complex [iodine atom I(1)] and the complex positioned at the centre of symmetry [iodine atom I(2)].

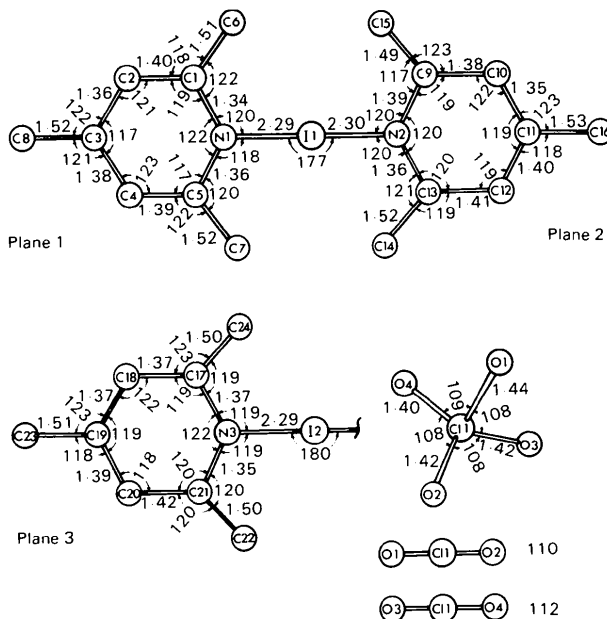


Fig. 2. Bond distances (\AA) and interbond angles ($^\circ$) with atom numbering. The estimated errors in these parameters average 0.01 \AA for bond lengths and 1° for angles. The Cl(2)-O distances for the disordered perchlorate are: O(5) $1.32 (5)$, O(6) $1.51 (2)$, O(7) $1.41 (6)$, O(8) $2.1 (2) \text{ \AA}$. The angles involving O(5), O(6) and Cl(2) are only approximately tetrahedral: range $102-116^\circ$.

the bis(3-picolyliodonium cation it is 2.24 Å (Osborn, 1972). It has been suggested that these latter two distances are shorter than those observed for tertiary amines; *e.g.* in the bis(hexamethylenetetramine)-iodonium cation the distance is 2.30 Å (Pritzkow, 1975). It would appear that the bulky methyl groups at the 2,6 positions of the pyridine ring have caused the twist and slip conformations and the increased bond length from that in pyridine. $2I_2$.

This is not due, however, to steric hindrance between methyl groups, as the distances C(6)···C(15), C(7)···C(14) and C(22)···C(24') are 4.67, 4.57 and 4.40 Å respectively. Even with the two γ -collidine rings exactly coplanar the minimum contact distance is 4.19 Å, a value comfortable enough to accommodate two methyl groups with van der Waals radii of ~ 2.0 Å.

The fact that the iodine atoms lie out of the γ -collidine ring planes (Table 2) indicates that a close intramolecular contact between the bulky iodonium cation (radius ≈ 2.0 Å) and the methyl groups (van der Waals radius ≈ 2.0 Å; Bondi, 1964) exists and precludes a coplanar arrangement. There are six unique CH₃···I intramolecular non-bonded contacts in the two cations of average length 3.315 Å, approximately 0.7 Å shorter than the sum of the van der Waals radii.

The two bond angles at the iodine atoms I(1) and I(2) are 177 (1) and 180°, respectively. A linear or nearly linear bond angle at the iodine has been observed frequently; for example 180° in the dipyridyliodonium cation (Hassel & Hope, 1961), 179° in pyridine·ICl (Rømming, 1972), 180° in 4-picoline·I₂ (Hassel, Rømming & Tufte, 1961), 176° in trimethylamine·ICl (Hassel & Hope, 1960), 180° in trimethylamine·I₂ (Strømme, 1959) and 176.5° in bis(hexamethylenetetramine)iodonium triiodide (Pritzkow, 1975).

Table 2. *Least-squares planes and distances therefrom*

(a) Equations

Plane	<i>p</i>	<i>q</i>	<i>r</i>	<i>d</i>	χ^2
1	0.8532 <i>x</i>	+0.1581 <i>y</i>	-0.4970 <i>z</i>	= -2.4371	2.01
2	0.8465 <i>x</i>	-0.4281 <i>y</i>	-0.3166 <i>z</i>	= -1.4564	0.99
3	0.8467 <i>x</i>	+0.3893 <i>y</i>	-0.3627 <i>z</i>	= 2.8216	6.50

(b) Distances (Å) of atoms from least-squares planes

Plane 1		Plane 2		Plane 3	
N(1)*	0.012 (8)	N(2)*	-0.005 (8)	N(3)*	-0.029 (9)
C(1)*	-0.008 (9)	C(9)*	0.001 (9)	C(17)*	0.015 (10)
C(2)*	0.006 (9)	C(10)*	-0.002 (10)	C(18)*	0.008 (11)
C(3)*	-0.008 (10)	C(11)*	0.007 (12)	C(19)*	-0.015 (11)
C(4)*	0.012 (9)	C(12)*	-0.011 (11)	C(20)*	0.002 (12)
C(5)*	-0.014 (10)	C(13)*	0.010 (10)	C(21)*	0.020 (10)
C(6)	0.041 (11)	C(14)	0.012 (10)	C(22)	0.091 (12)
C(7)	-0.006 (12)	C(15)	0.021 (11)	C(23)	-0.022 (11)
C(8)	0.034 (11)	C(16)	0.020 (11)	C(24)	0.080 (12)
I(1)	-0.142 (6)	I(1)	-0.262 (6)	I(2)	-0.674 (7)

* Atoms used to define the least-squares plane.

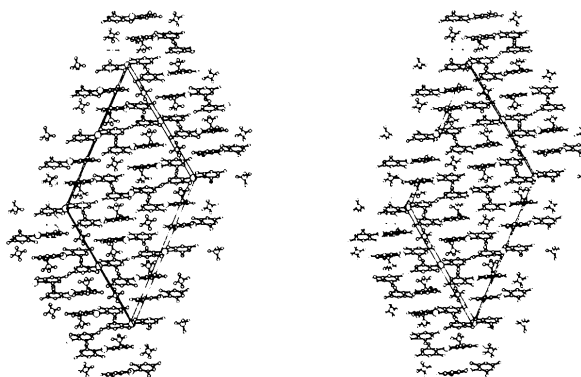


Fig. 3. Partial packing diagram for bis(2,4,6-trimethyl-1-pyridyl)-iodonium perchlorate showing the stacking of the ring planes. The perchlorate ions interleave the planes to provide the counterion to the iodonium cation. The three unique interplanar spacings are 3.61, 3.84 and 3.50 Å.

A partial packing diagram is shown in Fig. 3. There are six γ -collidine rings which stack so that there are three unique distances between planes. The distances are: plane 1 to plane 1 stacked across a centre of symmetry, 3.61 Å; plane 1 to plane 3 [these planes have a dihedral angle of 15°, so a mean distance is given by C(19) in plane 3 to plane 1 of 3.84 Å]; plane 2 to plane 3, 3.50 Å. The stacking of these planes is clearly an important determinant in the crystal packing which has interleaving perchlorate anions as counterions to the positively charged iodonium cations.

It is difficult to judge whether the presence of the *ortho*-methyl groups has caused the observed lengthening of the I-N charge-transfer bond length from an expected ~ 2.16 Å (Hassel & Hope, 1961). However, it is clear that these bulky groups have brought about alterations in the molecular conformations which could be due to the short intracationic non-bonded interaction between the iodine and methyl groups.

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X-ray Analysis of 3,4-Dihydro-2*H*-[1]benzothieno[3,2-*b*]pyran-2-spiro-2'(3'*H*)-(1-benzothiophen)-3'-one

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Abstract. C₁₈H₁₂O₂S₂, *M_r* = 324.4, *D_x* = 1.443 Mg m⁻³, monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 9.722 (4), *b* = 12.982 (16), *c* = 11.991 (6) Å, β = 99.40 (4)°, *U* = 1493.1 Å³, μ(Mo *K*α) = 0.307 mm⁻¹. Final *R* = 0.050 for 1695 independent reflexions. The dimer is spiro-fused and contains benzothiophene moieties that are almost planar, together with a central dihydropyran ring that adopts a half-chair conformation.

Introduction. An X-ray analysis of the title compound was undertaken to determine the constitution of the molecule. As previously reported (Cox, MacKenzie & Thomson, 1981), it is formed by reaction of 3-bromothiochroman-4-one with sodium acetate in acetic acid. Data were obtained for a yellow, needle-shaped crystal from a Nicolet P3 automated diffractometer using monochromatized Mo *K*α radiation. Integrated relative intensities for 2366 independent reflexions with 2θ < 50° were measured as θ–2θ scans; 1695 reflexions had *I* > 2.5σ(*I*).

The crystal structure was elucidated by direct phasing using the program *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms were located (near calculated positions) on electron density maps calculated at intermediate stages of structure refinement. In the final cycles of full-matrix

least-squares refinement the positional parameters for all atoms, anisotropic thermal parameters for the C and O atoms and isotropic thermal parameters for the H atoms were varied. A unit weighting scheme was used and convergence was reached at *R* = 0.050.

Discussion. The molecular structure and the packing of the molecules in the unit cell are shown in Figs. 1 and 2. The atomic coordinates are listed in Table 1 and the bond lengths, valency angles and torsion angles are in Tables 2–4.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36234 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

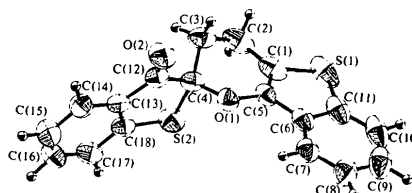


Fig. 1. The atomic arrangement in the molecule.