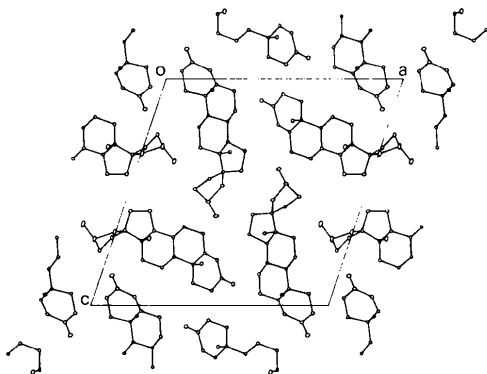


Tableau 2. *Contacts de van der Waals courts, $\bar{\sigma}$ pour les distances: 0,02 Å*

S(20A)—O(20A)···H(6A)—C(6B) (<i>x, y, z</i>) (1 - <i>x</i> , $\frac{1}{2} + y$, 1 - <i>z</i>)	O(20A)···H(6A)	2,43 Å	S(20A)—O(20A)···H(6A)	130°
			O(20A)···H(6A)—C(6B)	157
S(20A)···H(6B)—C(6B) (<i>x, y, z</i>) (1 - <i>x</i> , $y - \frac{1}{2}$, 1 - <i>z</i>)	S(20A)···H(6B)	2,80	C(21A)—S(20A)···H(6B)	146
			O(17A)—S(20A)···H(6B)	119
			O(20A)—S(20A)···H(6B)	74
			S(20A)···H(6B)—C(6B)	140
S(20B)—O(20B)···H(22E)—C(22A) (<i>x, y, z</i>) (1 + <i>x</i> , <i>y, z</i>)	O(20B)···H(22E)	2,53	S(20B)—O(20B)···H(22E)	142
			O(20B)···H(22E)—C(22A)	135

Fig. 4. Projection de la structure selon l'axe *b*.

orientations des liaisons S→O pour les deux isomères RU22454 et RU22479 observées lors de cette étude sont en accord avec les prévisions obtenues par voie physicochimique.

La Fig. 4 montre l'organisation cristalline. La cohésion est assurée par des contacts de van der Waals dont trois sont courts (Tableau 2).

L'auteur remercie la Société Roussel-Uclaf et en particulier M R. Bucourt et M L. Nedelec de lui avoir proposé cette étude et fourni un échantillon de RU22479.

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Structure of *p,p'*-Dichlorodithiooxanilide

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Abstract. C₁₄H₁₀Cl₂N₂S₂, *M_r* = 341.27, monoclinic, red needles, *P*2₁/*n*, *a* = 19.169 (3), *b* = 4.083 (1), *c* = 19.412 (3) Å, β = 103.11 (1)°; *D_x* = 1.531 Mg m⁻³ for *Z* = 4. Crystals consist of two independent centrosymmetric molecules, which differ slightly in their bond angles and conformations.

Introduction. The dipole moment of the present compound is 1.03 D (3.44 × 10⁻³⁰ Cm) in benzene solution (Katagiri, Kudo & Yamada, 1978). This indicates that there must be some distortion from a centrosymmetric structure. The present study was undertaken in order to investigate this possible distortion.

Intensity data were collected with graphite-monochromated Mo *K*α radiation on a Rigaku four-circle automatic diffractometer using a crystal of dimensions 0.2 × 0.25 × 0.3 mm. The θ–2θ scan was used for a range of (1.0 + 0.35 tan θ)°, the scan speed being 4° min⁻¹ in 2θ. Four standard reflexions showed only statistical fluctuations throughout the data collection. The intensities were corrected for Lorentz–polarization effects, but not for absorption, μ(Mo *K*α) = 0.698 mm⁻¹. A total of 3190 independent reflexions with 2θ < 54.0° were measured; 2308 with |*F_o*| ≥ 3σ(*F_o*) were considered as observed and were used in the refinement.

The structure was determined using *MULTAN* (Germain, Main & Woolfson, 1971). Block-diagonal-matrix least-squares refinement was followed by a difference Fourier synthesis which revealed all the H atoms. The final *R* was 0.072 for the observed reflexions and 0.124 for all reflexions. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme used was $w = 1/[\sigma^2(F_o) + 0.02608|F_o| - 0.00001|F_o|^2]$ for the observed reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic parameters obtained are given in Table 1.*

Discussion. The crystal consists of two independent molecules, (1) and (2), centred on crystallographic centres of symmetry at 0,1,0 and $\frac{1}{2},0,0$, respectively. Although the corresponding bond lengths are nearly equal (Fig. 1), significant differences are observed in bond angles and the planarity of the molecule (Table 2).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34427 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates* ($\times 10^4$ for the non-hydrogen atoms, $\times 10^3$ for H) *with their estimated standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
Cl(1)	3757 (1)	4497 (5)	1811 (1)
S(1)	203 (1)	11393 (4)	1102 (1)
N(1)	872 (2)	8326 (11)	207 (2)
C(11)	1548 (2)	7477 (13)	636 (2)
C(12)	1980 (2)	5605 (13)	298 (2)
C(13)	2660 (3)	4699 (14)	658 (3)
C(14)	2901 (2)	5650 (14)	1347 (3)
C(15)	2481 (3)	7456 (14)	1693 (3)
C(16)	1797 (3)	8397 (14)	1339 (3)
C(17)	302 (2)	9877 (13)	337 (2)
Cl(2)	6970 (1)	4897 (4)	3692 (1)
S(2)	6082 (1)	1453 (5)	25 (1)
N(2)	5202 (2)	1025 (11)	907 (2)
C(21)	5645 (2)	2049 (12)	1560 (2)
C(22)	5430 (2)	1068 (13)	2170 (2)
C(23)	5837 (3)	1951 (14)	2825 (2)
C(24)	6445 (2)	3822 (13)	2867 (2)
C(25)	6654 (2)	4850 (13)	2272 (2)
C(26)	6252 (3)	3991 (13)	1603 (3)
C(27)	5326 (2)	676 (12)	268 (2)
H(1)	81 (3)	764 (14)	-26 (3)
H(12)	180 (2)	486 (13)	-21 (2)
H(13)	294 (2)	347 (13)	38 (2)
H(15)	264 (3)	805 (14)	220 (3)
H(16)	149 (3)	968 (13)	159 (3)
H(2)	475 (3)	27 (14)	93 (3)
H(22)	501 (3)	-22 (14)	214 (3)
H(23)	569 (3)	121 (13)	327 (3)
H(25)	706 (3)	629 (15)	230 (3)
H(26)	640 (3)	472 (15)	119 (3)

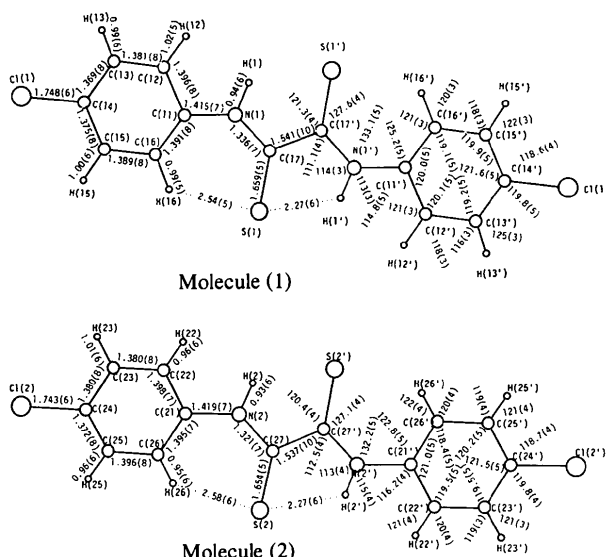


Fig. 1. Bond distances (Å) and angles (°).

Table 2. *Deviations* (Å) *of atoms from the least-squares planes*

An asterisk denotes atoms used to calculate the plane.

Plane 1	Plane 2	Plane 3	Plane 4
C(11) -0.005*	S(1) 0.000*	C(21) 0.011*	S(2) 0.000*
C(12) 0.004*	N(1) 0.000*	C(22) -0.007*	N(2) 0.000*
C(13) 0.002*	C(17) 0.000*	C(23) -0.001*	C(27) 0.000*
C(14) -0.005*	Cl(1) -0.076	C(24) 0.006*	Cl(2) 0.238
C(15) 0.004*	C(11) -0.002	C(25) -0.002*	C(21) 0.025
C(16) 0.002*	C(12) 0.102	C(26) -0.007*	C(22) 0.483
Cl(1) 0.005	C(13) 0.075	Cl(2) 0.038	C(23) 0.545
S(1) 0.171	C(14) -0.052	S(2) 0.986	C(24) 0.139
N(1) -0.041	C(15) -0.139	N(2) 0.015	C(25) -0.335
C(17) 0.020	C(16) -0.117	C(27) 0.393	C(26) -0.408
	C(17') 0.011		C(27') 0.033

Equations of the planes are $AX + BY + CZ + D = 0$ in which *X*, *Y* and *Z* are Cartesian coordinates in Å referred to *a*, *b* and *c*^{*}, respectively.

Plane	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
1	-0.4515	-0.8404	0.3000	3.412
2	-0.4349	-0.8742	0.2160	3.575
3	0.5573	-0.8300	0.0247	-5.014
4	0.2574	-0.9405	0.2218	-2.450

The C(17)–C(17') and C(27)–C(27') distances are significantly longer than usual for C(*sp*²)–C(*sp*²) single bonds. Since the corresponding bonds in oxamide (Ayerst & Duke, 1954) and dithiooxamide (Wheatley, 1965) are also longer, this elongation appears to be characteristic of these systems.

The C=S distances are close to those in dithiooxamide (Wheatley, 1965), but are significantly shorter than those in thioacetamide (Truter, 1960), dithio-biurea (Pignedoli, Peyronel & Antolini, 1975), and 1-thiocarbamoylimidazolidine-2-thione (Valle, Cojazzi, Busetti & Mammi, 1970). These shorter distances relate to the smaller bond angles opposite the S atom.

The C(17)—N(1) and C(27)—N(2) lengths are close to those in related amide groups (Pignedoli *et al.*, 1975) and in the peptide bond (Pauling, 1960). The thioamide groups are strictly planar. The C(11)—N(1) and C(21)—N(2) lengths are nearly equal to that in acetanilide (Brown, 1966).

The intramolecular S(1)···N(1') and S(2)···N(2') distances are 2·888 and 2·887 Å, with S···H distances of 2·27 Å, and N—H···S angles of 123 and 122° respectively. The H(1) and H(2) positions located in the final difference map show no tendency to deviate from the S(1), C(17), C(17'), N(1') plane and its equivalent in molecule (2) respectively, indicating the trigonal hybridization of the N atoms.

A significant difference between molecules (1) and (2) is found in the torsion angles; C(16)—C(11)—N(1)—C(17) is 5·7 (9)° and C(26)—C(21)—N(2)—C(27) 23·3 (9)°. The former value is very much smaller than that of 20·0° in acetanilide (Brown, 1966). The enhanced planarity of molecule (1) appears to be achieved at the expense of bond-angle strain about N(1) and C(11). S(1)···H(16) and S(2)···H(26) are significantly shorter than the sum of the van der Waals radii. There are no unusually close contacts between the molecules.

Contrary to expectation, the crystal structure does not directly explain the dipole moment mentioned above. However, three possibilities may be considered: rotations about the central C—C and amide C—N bonds, and a hybridization change for N to *sp*³. The

last two may be rejected, since the C—N lengths show considerable double-bond character. Therefore, the structure in solution probably has some rotation about the central C—C bond owing to the intramolecular steric repulsion between S(1) and H(1'). The centrosymmetric conformation in the crystal may be due to the crystal-field effect.

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2,2'-Bichinolinium-dijodtrichlorid

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Abstract. C₁₈H₁₃N₂⁺.Cl₃I₂⁻, orthorhombic, *Pbcn*, *a* = 4·532 (2), *b* = 22·773 (6), *c* = 19·729 (6) Å, *Z* = 4, *V* = 2036 Å³, *D_c* = 2·01 Mg m⁻³. The crystal structure has been determined from three-dimensional single-crystal X-ray data; the final *R* value is 0·024 for 2027 reflexions. The I₂Cl₃⁻ anion is *V*-shaped like the pentaiodide ion I₅⁻. The I—Cl distances are 2·718 (2) Å for the bridging Cl and 2·417 (2) Å for the terminal Cl atoms. The proton of the biquinolinium cation is disordered and coordinated alternatively to either of the two N atoms.

Einleitung. Neben den seit langem bekannten Pentahalogenidanionen der Typen Y₅⁻ und XY₄⁻ sind seit einiger Zeit auch stabile Verbindungen der Zusammensetzung X₂Y₃⁻ zugänglich (Yagi & Popov, 1967). Im Gegensatz zu den beiden erstgenannten Anionentypen, deren Molekülstrukturen röntgenografisch ermittelt sind (I₅⁻: *V*-förmig gewinkelt; ICl₄⁻: quadratisch planar), war die Struktur des Typs X₂Y₃⁻ bisher unbekannt. Zur Diskussion der Molekülstruktur standen lediglich IR-Spektren und der Syntheseweg zur Verfügung. Verbindungen mit dem Dijodtrichloridanion I₂Cl₃⁻ entstehen