

transfer complex. In particular, the C—S distances in the DTT1 complex are slightly longer in the inner thiophene ring [1.74 (1) Å average] than in the outer rings [1.70 (1) Å average] as observed to a similar extent for DTT [averaged values 1.756 (1) and 1.704 (1) Å respectively]. The π delocalization of the C—S bond is presumably smaller in the central ring. Further similarities between DTT1 in the complex and as a free molecule are detected by comparing the C—C distances: the difference between average 'double' and 'single' bonds is smaller in the central ring than in the outer rings.

The relatively low overall accuracy of the present crystal structure determination, due mainly to crystal quality, does not allow the discussion of finer details.

The TCNQ residue is planar, in fact the two dicyanomethylene-group best planes are bent only 0.6 (2) and 1.3 (2)° out of the quinonoid ring plane. The corresponding values found in the DTT–TCNQ complex are 1.2 (1) and 2.3 (1)° respectively. The C—C—N groups are all strictly linear and the C—C double bond connecting the cyano group and the quinonoid ring is 1.38 (1) Å (average), compared with 1.383 Å found in the DTT charge-transfer complex. The dimensions of the TCNQ molecule closely resemble those observed in the DTT complex (Bettinelli *et al.*, 1984, and references therein).

As both donor and acceptor molecules lie at a general position in the crystal (space group $P2_1/c$), the contacts between a molecule and two adjacent ones in the stack are not equivalent. In fact, the distances of TCNQ atoms at x, y, z and at $1+x, y, z$ to the least-squares plane of DTT1 range from 3.28 to 3.56 Å (av. 3.38 Å) and from 3.31 to 3.58 Å (av. 3.49 Å), respectively. The partial dimerization

observed in the DTT–TCNQ complex is also detected in this case, although to a lesser extent. The shorter contact in the stack is 3.40 Å from S3 to C10. The molecular packing is governed by the short contacts involving adjacent molecules of TCNQ [$N3 \cdots N3^i (-x, -y, 1-z)$ 3.235 (8) Å], or of DTT1 and TCNQ [$S2 \cdots N4^{ii} (x, 1+y, 1+z)$ 3.370 (5) Å].

In conclusion, we remark that all the structural evidence strongly indicates that DTT1–TCNQ is a low-ionicity charge-transfer complex, as expected from comparison with the analogous DTT–TCNQ and oligothiophene-containing charge-transfer complexes (Hotta & Waragai, 1989). The DC conductivity measured on a 'single' crystal ($\sigma_{239K} = 2 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$) confirmed the above conclusions.

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Azoles. 29.* Structure of the Molecular Complex of 3,5-Dinitroindazole with Piperazine and Water (2/1/2)

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Abstract. $C_4H_{12}N_2^{2+} \cdot 2C_7H_3N_4O_4^- \cdot 2H_2O$, $M_r = 538.43$, monoclinic, $P2_1/c$, $a = 12.818$ (3), $b = 13.769$ (4), $c = 6.701$ (1) Å, $\beta = 104.60$ (2)°, $V =$

1144.5 (5) Å³, $Z = 2$, $D_m = 1.56$ (1), $D_x = 1.56 \text{ Mg m}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu(\text{Cu } K\alpha) = 1.005 \text{ mm}^{-1}$, $F(000) = 560$, room temperature, final $R = 0.035$ for 1209 observed reflections. The piperazine ring lies on the centre of symmetry. Piperazine forms a double $H_2N^+ \leftarrow$ ammonium cation as a

* Part 28: Gzella & Wrzeciono (1990).

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.			
	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	0.2542 (2)	0.5112 (2)	0.7605 (3)
N(2)	0.3079 (2)	0.4301 (2)	0.7320 (3)
C(3)	0.2402 (2)	0.3547 (2)	0.7109 (4)
C(4)	0.0361 (2)	0.3402 (2)	0.7021 (4)
C(5)	-0.0462 (2)	0.4010 (2)	0.7162 (4)
C(6)	-0.0343 (2)	0.5018 (2)	0.7519 (4)
C(7)	0.0636 (2)	0.5435 (2)	0.7707 (4)
C(8)	0.1504 (2)	0.4846 (2)	0.7548 (4)
C(9)	0.1367 (2)	0.3829 (2)	0.7227 (4)
N(10)	0.2785 (2)	0.2600 (2)	0.6839 (3)
O(11)	0.3684 (1)	0.2507 (1)	0.6506 (3)
O(12)	0.2187 (2)	0.1910 (1)	0.6956 (3)
N(13)	-0.1546 (2)	0.3600 (2)	0.6847 (4)
O(14)	-0.1710 (2)	0.2783 (2)	0.6084 (4)
O(15)	-0.2248 (2)	0.4078 (2)	0.7304 (3)
N(16)	0.5201 (2)	0.4334 (2)	0.6695 (4)
C(17)	0.5228 (2)	0.4003 (2)	0.4598 (4)
C(18)	0.5508 (2)	0.5384 (2)	0.7022 (5)
O(19)	0.3739 (2)	0.6647 (1)	0.9708 (3)

Table 2. Bond distances (\AA) and angles ($^\circ$) and their standard deviations

N(1)—N(2)	1.351 (3)	C(7)—C(8)	1.403 (4)
N(1)—C(8)	1.371 (3)	C(8)—C(9)	1.421 (3)
N(2)—C(3)	1.336 (3)	N(10)—O(11)	1.234 (3)
C(3)—C(9)	1.404 (3)	N(10)—O(12)	1.236 (3)
C(3)—N(10)	1.421 (3)	N(13)—O(14)	1.232 (3)
C(4)—C(5)	1.367 (4)	N(13)—O(15)	1.215 (3)
C(4)—C(9)	1.393 (3)	N(16)—C(17)	1.486 (3)
C(5)—C(6)	1.410 (4)	N(16)—C(18)	1.500 (3)
C(5)—N(13)	1.466 (3)	C(17)—C(18')	1.505 (3)
C(6)—C(7)	1.357 (4)		
N(2)—N(1)—C(8)	107.5 (2)	N(1)—C(8)—C(9)	110.5 (2)
N(1)—N(2)—C(3)	108.5 (2)	C(4)—C(9)—C(8)	120.4 (2)
N(2)—C(3)—N(10)	119.4 (2)	C(3)—C(9)—C(8)	101.4 (2)
N(2)—C(3)—C(9)	112.1 (2)	C(3)—N(10)—O(12)	117.2 (2)
C(9)—C(3)—N(10)	128.5 (2)	C(3)—N(10)—O(11)	119.1 (2)
C(5)—C(4)—C(9)	116.5 (3)	O(11)—N(10)—O(12)	123.7 (2)
C(4)—C(5)—N(13)	118.3 (2)	C(5)—N(13)—O(15)	119.4 (3)
C(4)—C(5)—C(6)	124.2 (3)	C(5)—N(13)—O(14)	117.9 (3)
C(6)—C(5)—N(13)	117.4 (2)	O(14)—N(13)—O(15)	122.7 (3)
C(5)—C(6)—C(7)	119.3 (3)	C(17)—N(16)—C(18)	111.4 (2)
C(6)—C(7)—C(8)	118.8 (3)	N(16)—C(17)—C(18')	110.5 (2)
C(7)—C(8)—C(9)	120.7 (2)	N(16)—C(18)—C(17')	110.0 (2)

Symmetry code: (i) $1-x, 1-y, 1-z$.Table 3. Hydrogen bonds (\AA and $^\circ$)

	<i>D</i> ... <i>A</i>	<i>H</i> ... <i>A</i>	\angle <i>D</i> — <i>H</i> ... <i>A</i>
N(16)—H(162)...N(2)	2.855 (3)	1.86 (3)	171 (2)
N(16 ⁱⁱ)—H(161 ⁱⁱ)...O(19)	2.798 (3)	1.86 (3)	163 (2)
O(19)—H(191)...N(1)	2.778 (3)	1.83 (3)	172 (3)
O(19)—H(192)...O(14 ⁱⁱⁱ)	2.965 (3)	2.08 (4)	155 (3)

Symmetry code: (ii) $1-x, 1-y, 2-z$; (iii) $-x, 0.5+y, 1.5-z$.

result of the incorporation of two protons from the pyrrole N(1) and N(1') [(i) $1-x, 1-y, 1-z$] nitrogen atoms. The indazole system is slightly folded, the maximum deviation [atom C(9)] from the least-squares plane being 0.034 (3) \AA . The piperazinium cation has a chair conformation and forms a dihedral angle of 85.1 (1) $^\circ$ with the indazole system. The crystal lattice contains an infinite three-dimensional network of hydrogen bonds, in which the water molecules exhibit both donor and acceptor functions.

Introduction. This paper is devoted to the structure of a molecular complex of 3,5-dinitroindazole with piperazine. For the preparation of this compound, 3,5-dinitroindazole was treated with piperazine according to Wrzeczono & Linkowska (1980). The structures of other molecular complexes of 3,5-dinitroindazole with cyclic amines have been described by Gzella, Wrzeczono & Borowiak (1989) and Gzella & Wrzeczono (1990).

Experimental. Yellow plate crystals were recrystallized from water, m.p. 481–483 K, D_m by flotation, crystal dimensions 0.5 \times 0.3 \times 0.1 mm, Syntex $P2_1$ diffractometer, graphite-monochromated Cu $K\alpha$ radiation, accurate cell parameters were refined from setting angles of 15 reflections with $18.9^\circ \leq 2\theta \leq 31.2^\circ$, θ - 2θ scan technique, two standard reflections were monitored every 100 reflections, no significant intensity variation, profiles measured for 1721 reflections with $2\theta \leq 115^\circ$, 1506 unique reflections, $R_{int} = 0.045$, range of hkl : $h - 13$ to 13 , $k 0$ to 14 , $l 0$ to 7 , profile analysis was according to Lehmann & Larsen (1974), no absorption correction, 1209 reflections with $I \geq 1.96\sigma(I)$ were considered observed in the refinement, structure solved by direct methods

using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refinement on F by full-matrix least-squares method, 217 refined parameters, hydrogen atoms were generated from ΔF map and refined with isotropic temperature parameters, $w^{-1} = \sigma^2(F)$, empirical isotropic extinction parameter x was used to correct F_c according to $F'_c = F_c(1 - 0.0001xF_c^2/\sin\theta)$, x converged to 0.0173 (8), final $R = 0.035$ and $wR = 0.037$, $S = 3.492$, $(\Delta/\sigma)_{max} = 0.03$, $-0.19 \leq \Delta\rho \leq 0.15$ e \AA^{-3} . Computer programs: *SHELX76* (Sheldrick, 1976) and local programs (Jaskolski, 1982), molecular illustrations were drawn using *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors were from *SHELX76*.

Discussion. The final atomic coordinates are given in Table 1. Bond distances and angles are given in Table 2.* The labelling system is shown in Fig. 1. A stereoview of the molecular structure is presented in Fig. 2. The piperazine molecule lies on the centre of

* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53254 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

symmetry. Piperazine makes a double $\text{H}_2\text{N}^+ \leftarrow$ ammonium cation as a result of the incorporation of two protons from the nitrogen atoms N(1) and N(1ⁱ) [(i) 1 - x, 1 - y, 1 - z] of the indazole moieties. The N—H bond distances are N(16)—H(161) 0.96 (3) and N(16)—H(162) 1.00 (3) Å. The indazole system is slightly folded, the maximum deviation [atom C(9)] from its least-squares plane is 0.034 (3) Å. The piperazinium cation has a chair conformation, the least-squares plane through it makes a dihedral angle of 85.1 (1)° with the indazole system. Molecules in the crystal lattice are hydrogen bonded (Table 3), forming an infinite three-dimensional lattice of hydrogen bonds (Figs. 3a and 3b), in which the water molecules exhibit both donor and acceptor functions.

The values of the bond parameters for the indazole system are similar to those observed for the indazolate anion, [ind]⁻, of the 2/1 molecular complex of 3,5-dinitroindazole with morpholine (Gzella *et al.*, 1989) or of the 1/1 molecular complex of 3,5-dinitroindazole with pyrrolidine (Gzella & Wrzeciono, 1990). The plane of the nitro group attached to C(5) is inclined by 14.8 (1)° to the plane of the indazole system. This distortion from planarity, resulting from a rotation around the C(5)—N(13) bond, is probably caused by the hydrogen bond O(14ⁱⁱⁱ)...O(19) (Table 3). The exocyclic bond

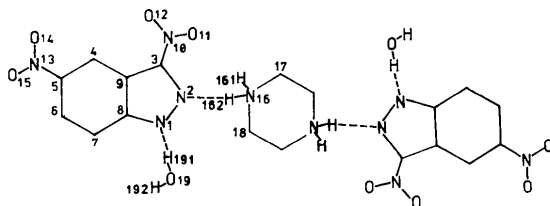


Fig. 1. Labelling scheme.

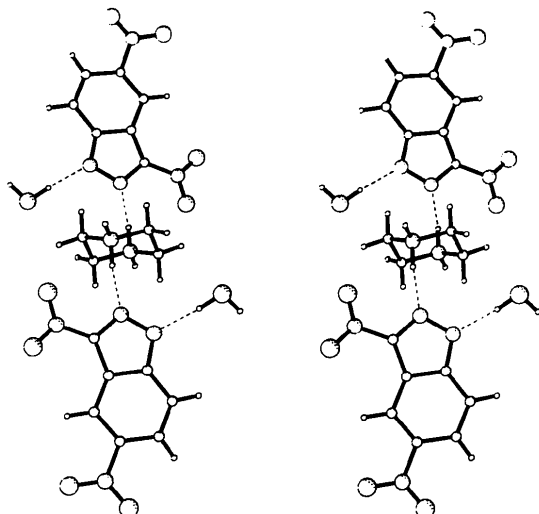


Fig. 2. Stereodrawing of the molecule.

C(3)—N(10), 1.421 (3) Å, is shorter than the value of the single C—N bond, 1.468 (14) Å, reported by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987). The plane of the nitro group on C(3) makes a dihedral angle of 11.4 (1)° with the plane of the indazole system.

The bond lengths N(16)—C(17) [1.486 (3) Å] and N(16)—C(18) [1.500 (3) Å] in the piperazinium cation are not unusual when compared with the $\text{H}_3\text{N}^+ \text{—C}$ bond, 1.497 (3) Å (Nakai, 1988), or with the $\text{H}_2\text{N}^+ \text{—C}$ bond, 1.485 (5) Å (Gzella *et al.*, 1989). The C(17)—C(18ⁱ) [(i) 1 - x, 1 - y, 1 - z] bond distance [1.505 (3) Å] is somewhat shorter than the

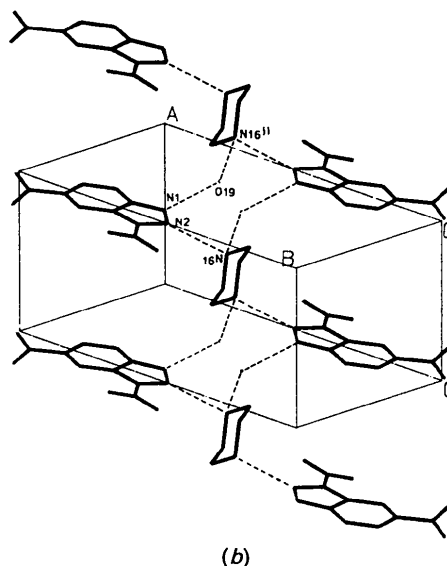
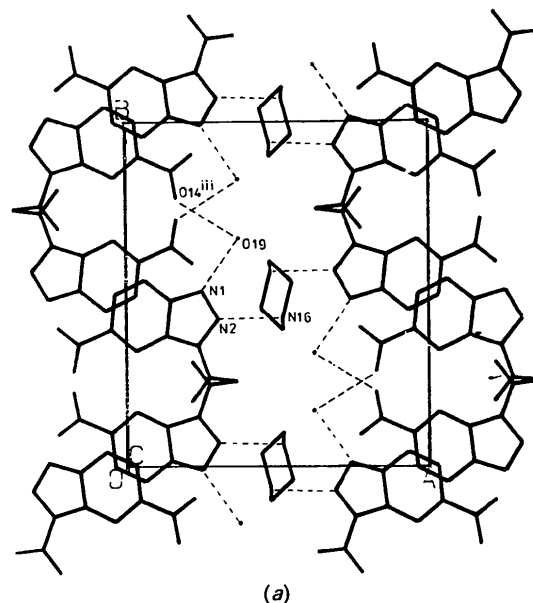


Fig. 3. (a) Molecular packing and hydrogen bonds in the unit cell, and (b) hydrogen bonds in the crystal lattice.

overall value of the $C(sp^3)-C(sp^3)$ bond length, 1.530 (15) Å (Allen *et al.*, 1987).

The molecular packing in the unit cell is given in Fig. 3(a). The hydrogen bonds in the crystal lattice are shown by broken lines in Figs. 3(a) and 3(b).

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Structure du Chlorhydrate de (Diméthylamino méthyl)-2 Acrylophénone

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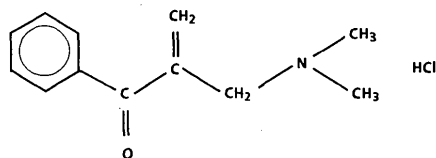
Abstract. (2-Benzoylallyl)dimethylammonium-chloride, $C_{12}H_{16}NO^+ \cdot Cl^-$, $M_r = 225.7$, $P2_1/c$, $a = 9.903$ (3), $b = 11.331$ (2), $c = 11.272$ (3) Å, $\beta = 98.18$ (3)°, $V = 1252$ (1) Å³, $Z = 4$, $D_x = 1.2$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 0.28$ mm⁻¹, $F(000) = 480$, $T = 298$ K, $R = 0.032$ for 1740 observed reflexions. Bond lengths and angles are in the usual range. The molecule is in an extended configuration; the aromatic plane forms a dihedral angle of 57 (1)° with the mean dimethylaminomethyl plane. Only one interionic hydrogen bond occurs in the structure involving the Cl^- ion and the N atom of the amine group. Molecular packing results from van der Waals interactions only.

Introduction. Les aminométhyl-2 acrylophénones constituent une famille d'agents antimicrotubulaires pour lesquels des propriétés antimicrobiennes, antifongiques, antiagrégantes plaquettaires et normolipémiants ont été démontrées (Lesieur, Lesieur, Lespagnol, Cazin, Mallevais & Delacourte, 1986).

Le site d'interaction de ces produits avec la tubuline est constitué par l'ensemble cétone α,β éthylénique dont la grande réactivité vis à vis des

nucléophiles permet la formation de liaisons covalentes avec des groupements sulfhydryles de la protéine et inhibe le formation des microtubules.

Cependant un certain nombre de questions restent posées quant à la spécificité de ces produits vis à vis de la tubuline et de certains groupements sulfhydryles (Luduena, Roach, Treka, Mallevais & Roie, 1987). La structure cristalline de l'un de ces dérivés, le chlorhydrate de (diméthylamino méthyl)-2 acrylophénone a été entreprise dans le but de préciser ses caractéristiques stériques et conformationnelles.



Partie expérimentale. Monocristaux en forme de parallélépipède préparés dans l'acétone, introduits dans un capillaire de Lindemann en quartz afin d'éviter la dégradation du produit pendant la mesure, diffractomètre quatre cercles Enraf-Nonius CAD-4, monochromateur au graphite, paramètres de