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2-(1,2-Dihydro-1-oxophthalazin-2-yl)-4,5-dihydroimidazolium Iodide and 2-(1,2-Dihydro-1-oxophthalazin-2-yl)-4,5,6,7-tetrahydro-1,3-diazepinium Iodide

MAREK L. GŁÓWKA^a AND WALDEMAR KSIĄŻEK^b

^a*Institute of General and Ecological Chemistry, Technical University of Łódź, Zwirki 36, 90-924 Łódź, Poland,* and ^b*Institute of Physics, Technical University of Łódź, Wólczańska 223, 90-924 Łódź, Poland. E-mail: mareklo@ck-sg.p.lodz.pl*

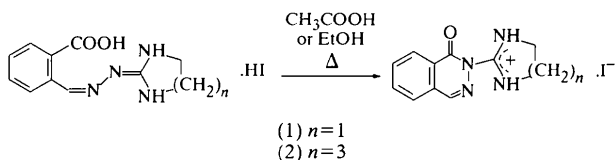
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Abstract

The molecular structures of the title compounds, C₁₁H₁₁N₄O⁺·I⁻ and C₁₃H₁₅N₄O⁺·I⁻, are very similar and thus display similar crystal packing and a similar hydrogen-bonding network. The coplanarity of the aromatic ring and the protonated amidine fragment of the saturated ring are due to conjugation of the two π-systems. Each I⁻ anion is surrounded by three neighboring molecules, all lying approximately in a plane. Anions participate in only one N—H···I⁻ hydrogen bond, with H···I distances of ~2.7 and 3.0 Å, and their coordination spheres are completed by weak C—H···I⁻ contacts.

Comment

The title compounds, 2-(1,2-dihydro-1-oxophthalazin-2-yl)-4,5-dihydroimidazolium iodide, (1), and 2-(1,2-dihydro-1-oxophthalazin-2-yl)-4,5,6,7-tetrahydro-1,3-diazepinium iodide, (2), were obtained by Krężel (1998) as products of an unexpected cyclization reaction of amidinehydrazones (see Scheme below). The unequivocal determination of their structures was carried out by X-ray diffraction methods.



Although seven 2-substituted 1-phthalazinones have been studied by X-ray diffraction (Cambridge Structural Database, 1997), none has a conjugated positively charged amidine-type substituent at N2 and thus they cannot be considered suitable reference compounds.

The positive charge of the protonated partially saturated imidazole (or diazepine) ring is spread over the entire conjugated N21—C22—N23 fragment, resulting in

equal C22—N endocyclic bond lengths (Tables 1 and 3). In addition, shortening of the exocyclic N2—C22 bond length from about 1.46 to 1.390 (6) and 1.422 (5) Å in (1) and (2), respectively, is observed due to conjugation of the phthalazinone system and the N—C—N π-system of the other ring. The resulting C1—N2—C22—N23 and N3—N2—C22—N21 torsion angles are -4.1 (7) and -0.5 (6)° in (1), and -5.0 (6) and -1.6 (5)° in (2). The O1 atom approaches the H atom at N23 forming an intramolecular hydrogen contact of 2.19 (6) Å. The same H atom, however, participates in a 'normal' hydrogen bond (N—H···O) with a molecule related by a center of symmetry, forming a dimer (Fig. 2). Each molecule of the dimer also makes a strong N21—H···I⁻ hydrogen bond, with an N···I⁻ distance of 3.534 (5) and 3.622 (4) Å, and an N—H···I⁻ angle of 150 (6) and 140 (5)°, in (1) and (2), respectively.

The similarity of the molecular shapes and hydrogen bonds in the studied structures results in similar crystal packing (Fig. 2) and similar unit-cell dimensions. After reduction, the cell angles for (2) are 102.57, 106.85 and 96.42°, compared with values of 100.92, 103.27 and 98.88° for (1).

The packing arrangements of molecules (1) and (2) in their respective crystals are determined by the arranging of planar dimers in hydrophobic belts, which in turn are separated by hydrophilic space filled with I⁻ anions. Each anion makes three contacts (N—H···I⁻ or C—H···I⁻) with surrounding approximately coplanar protonated molecules (Fig. 2).

In (1), in addition to the N21—H···I⁻ hydrogen bond, there are two distinct C—H···I⁻ contacts, with

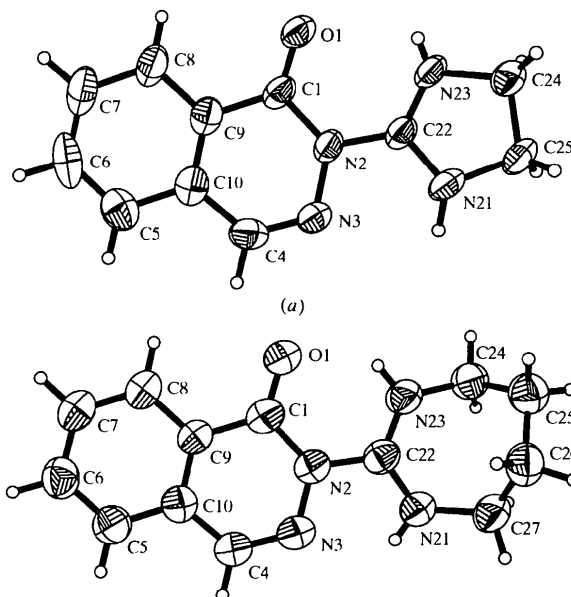


Fig. 1. ORTEP (Johnson, 1976) drawings of (a) (1) and (b) (2) showing their conformations and atom-labeling schemes. Displacement ellipsoids are drawn at the 50% probability level.

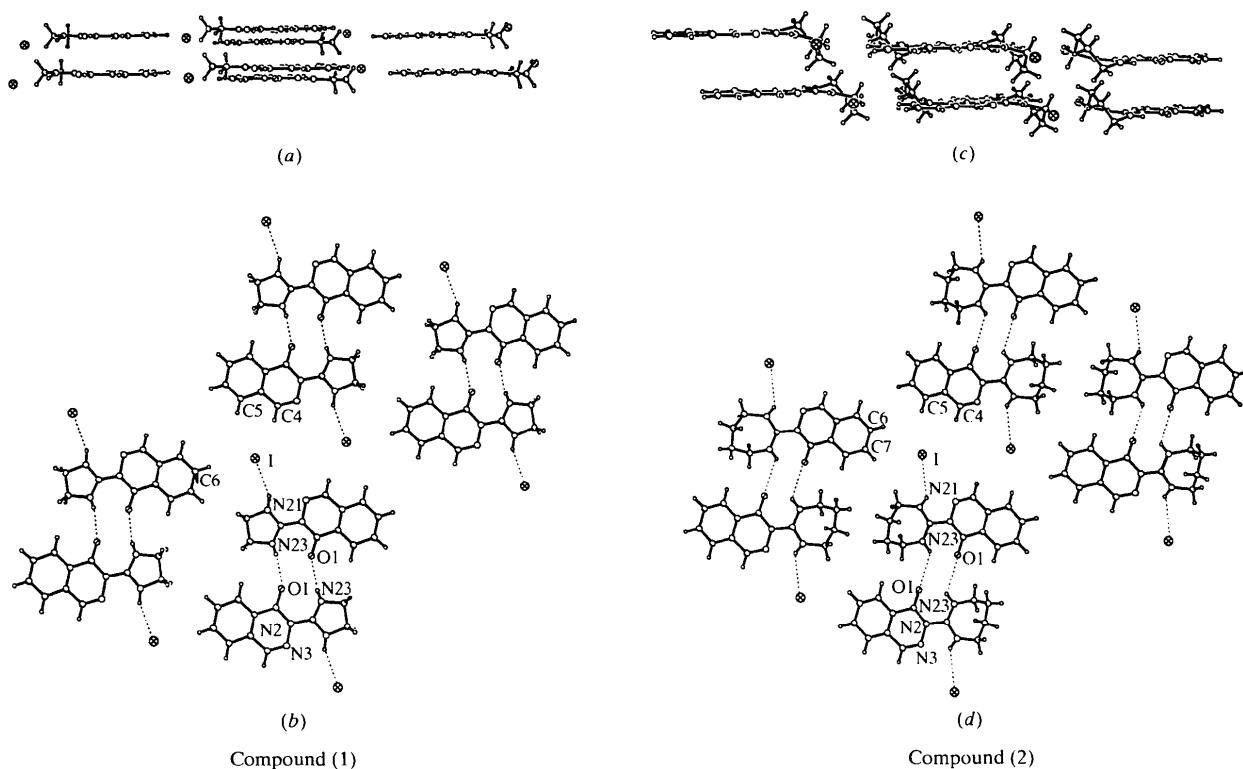


Fig. 2. Molecular packing and N—H···X (X = I or O) hydrogen bonds in structures (1) and (2); views (a) and (c) are parallel to the phthalazinone ring plane, and views (b) and (d) are perpendicular to the phthalazinone ring plane.

H···I distances of 3.10 (H6) and 3.11 Å (H4) (Table 2). As the molecule of (1) is generally planar and all three donor protons participating in hydrogen bonds lie approximately in a plane (the sum of the H···I···H angles is 348°), a two-dimensional network (layers) of hydrogen-bonded molecules is formed in these crystals. In (2), the tetrahydrodiazepine ring is significantly puckered (Figs. 1 and 2) and the planar arrangement of molecules in the crystal is hindered. The resulting packing of (2) differs from that of (1) by a slight twist around the center of symmetry and a parallel shift in opposite directions of molecules in the dimer to accommodate the larger tetrahydrodiazepine ring. In addition to the H atoms at N21, C6 and C4 of the three molecules surrounding I^- which form hydrogen contacts, three other H atoms (at C27, C7 and C5) approach the anion (Fig. 2b and Table 4).

Experimental

Crystals of (1) and (2) suitable for X-ray diffraction study were obtained from methanol solutions.

Compound (1)

Crystal data

$C_{11}H_{11}N_4O^+ \cdot I^-$
 $M_r = 342.14$

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$

Triclinic

$P\bar{1}$

$a = 7.303 (1) \text{ \AA}$
 $b = 8.583 (2) \text{ \AA}$
 $c = 10.489 (2) \text{ \AA}$
 $\alpha = 100.92 (3)^\circ$
 $\beta = 103.27 (3)^\circ$
 $\gamma = 98.88 (3)^\circ$
 $V = 614.7 (2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.848 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Kuma KM-4 diffractometer
 ω - 2θ scans
 Absorption correction:
 spherical (Kuma
 Diffraction, 1995)
 $T_{\min} = 0.070$, $T_{\max} = 0.213$
 2991 measured reflections
 2561 independent reflections
 2328 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.119$

Cell parameters from 62

reflections
 $\theta = 4-33^\circ$
 $\mu = 20.40 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Prism
 $0.28 \times 0.11 \times 0.11 \text{ mm}$
 Pale yellow

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 80.12^\circ$
 $h = -1 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -13 \rightarrow 13$
 3 standard reflections
 every 100 reflections
 intensity decay: 0.02%

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.112 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.817 \text{ e \AA}^{-3}$

$S = 1.062$
2561 reflections
173 parameters
H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0832P)^2 + 0.659P]$
where $P = F_o^2 + 2F_c^2/3$

Extinction correction:
SHELXL97
Extinction coefficient:
0.0012 (5)
Scattering factors from
International Tables for Crystallography (Vol. C)

$S = 1.092$
2968 reflections
195 parameters
H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0939P)^2 + 0.0714P]$
where $P = F_o^2 + 2F_c^2/3$

Extinction correction:
SHELXL97
Extinction coefficient:
0.0035 (6)
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (1)

O1—C1	1.209 (6)	N3—C4	1.275 (7)
C1—N2	1.395 (5)	N21—C22	1.307 (6)
N2—C22	1.390 (6)	C22—N23	1.303 (6)
N2—N3	1.416 (6)		
C22—N2—C1	122.4 (4)	C4—N3—N2	115.6 (4)
C22—N2—N3	111.3 (4)	N23—C22—N2	125.4 (4)
C1—N2—N3	126.1 (4)	N21—C22—N2	120.9 (4)
O1—C1—N2—C22	3.6 (7)	C1—N2—C22—N23	-4.1 (7)
C9—C1—N2—N3	-0.3 (7)	N3—N2—C22—N21	-0.5 (6)
C1—N2—N3—C4	0.8 (7)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$) for (1)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N23—H23 \cdots O1	0.73 (7)	2.19 (6)	2.632 (5)	121 (6)
N21—H21 \cdots I	0.87 (8)	2.75 (8)	3.534 (5)	150 (6)
N23—H23 \cdots O1 ⁱ	0.73 (7)	2.34 (7)	3.018 (5)	155 (6)
C4—H4 \cdots I ⁱⁱ	0.93	3.11	3.983 (5)	156.6
C5—H5 \cdots I ⁱⁱⁱ	0.93	3.52	4.287 (7)	141.9
C6—H6 \cdots I ⁱⁱⁱ	0.93	3.10	4.021 (5)	172.9

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $2 - x, 1 - y, 2 - z$; (iii) $x, y - 1, z - 1$.

Compound (2)*Crystal data*

$C_{13}H_{15}N_4O \cdot I^-$
 $M_r = 370.19$
Triclinic
 $P\bar{1}$
 $a = 8.196$ (2) \AA
 $b = 8.550$ (2) \AA
 $c = 10.787$ (2) \AA
 $\alpha = 77.43$ (3) $^\circ$
 $\beta = 73.15$ (3) $^\circ$
 $\gamma = 83.58$ (3) $^\circ$
 $V = 705.2$ (3) \AA^3
 $Z = 2$
 $D_x = 1.743$ Mg m^{-3}
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54178$ \AA
Cell parameters from 50 reflections
 $\theta = 23-31$ $^\circ$
 $\mu = 17.833$ mm^{-1}
 $T = 293$ (2) K
Prism
 $0.20 \times 0.14 \times 0.07$ mm
Pale yellow

Data collection

Kuma KM-4 diffractometer
 $\omega-2\theta$ scans
Absorption correction:
spherical (Kuma Diffraction, 1995)
 $T_{\min} = 0.125$, $T_{\max} = 0.368$
3183 measured reflections
2968 independent reflections
2650 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 80.99$ $^\circ$
 $h = -10 \rightarrow 10$
 $k = -1 \rightarrow 10$
 $l = -13 \rightarrow 13$
2 standard reflections every 100 reflections
intensity decay: 5.15%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.119$

$(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 1.125$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -1.405$ e \AA^{-3}

Table 3. Selected geometric parameters (\AA , $^\circ$) for (2)

O1—C1	1.220 (5)	N3—C4	1.292 (6)
C1—N2	1.403 (5)	N21—C22	1.308 (5)
N2—N3	1.391 (5)	C22—N23	1.308 (6)
N2—C22	1.422 (5)		
N3—N2—C1	124.5 (4)	C4—N3—N2	118.0 (4)
N3—N2—C22	111.4 (3)	N21—C22—N2	116.3 (4)
C1—N2—C22	124.1 (3)	N23—C22—N2	118.2 (4)
C9—C1—N2—N3	-1.2 (6)	N3—N2—C22—N21	-1.6 (5)
O1—C1—N2—C22	2.0 (7)	C1—N2—C22—N23	-5.0 (6)
C1—N2—N3—C4	0.2 (6)		

Table 4. Hydrogen-bonding geometry (\AA , $^\circ$) for (2)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N23—H23 \cdots O1	0.79 (6)	1.96 (5)	2.589 (5)	135 (5)
N21—H21 \cdots I	0.85 (6)	2.93 (6)	3.622 (4)	140 (5)
N23—H23 \cdots O1 ⁱ	0.79 (6)	2.74 (5)	3.274 (5)	126 (4)
C4—H4 \cdots I ⁱⁱ	0.93	3.40	4.237 (4)	151.7
C5—H5 \cdots I ⁱⁱⁱ	0.93	3.10	3.987 (5)	161.2
C6—H6 \cdots I ⁱⁱⁱ	0.93	3.32	3.983 (5)	129.8

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-1 - x, -y, 2 - z$; (iii) $x, 1 + y, z - 1$.

Intensities were corrected for crystal decay. H atoms at carbon were refined with C—H distances constrained to 0.96 \AA . The two N-bonded H atoms were refined freely with isotropic displacement parameters. The *SHELXTL/PC* program package (Sheldrick, 1990a) was used throughout the analysis. The $\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ values are greater than 1 e \AA^{-3} for the two reported structures due to the presence of the heavy I atom. The peaks are within 1.3 \AA of the I^- anion [all within 0.86 \AA except $\Delta\rho_{\text{max}}$ in (1)].

For both compounds, data collection: KM-4 software (Kuma Diffraction, 1995); cell refinement: KM-4 software; data reduction: *XDISK* in *SHELXTL/PC*; program(s) used to solve structures: *SHELXS97* (Sheldrick, 1990b); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1276). Services for accessing these data are described at the back of the journal.

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