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2,4-Dinitrophenylhydrazones of 2,4-dihydroxybenzaldehyde, 2,4-dihydroxyacetophenone and 2,4-dihydroxybenzophenone

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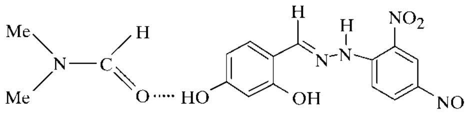
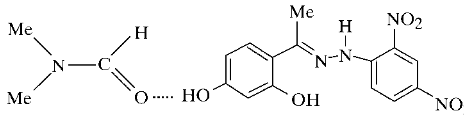
In 2,4-dihydroxybenzaldehyde 2,4-dinitrophenylhydrazone *N*,*N*-dimethylformamide solvate {or 4-[(2,4-dinitrophenyl)-hydrazonomethyl]benzene-1,3-diol *N*,*N*-dimethylformamide solvate}, $C_{13}H_{10}N_4O_6\cdot C_3H_7NO$, (X), 2,4-dihydroxyacetophenone 2,4-dinitrophenylhydrazone *N*,*N*-dimethylformamide solvate (or 4-{1-[(2,4-dinitrophenyl)hydrazono]ethyl}-benzene-1,3-diol *N*,*N*-dimethylformamide solvate), $C_{14}H_{12}N_4O_6\cdot C_3H_7NO$, (XI), and 2,4-dihydroxybenzophenone 2,4-dinitrophenylhydrazone *N*,*N*-dimethylacetamide solvate (or 4-{[(2,4-dinitrophenyl)hydrazono]phenylmethyl}benzene-1,3-diol *N*,*N*-dimethylacetamide solvate), $C_{19}H_{14}N_4O_6\cdot C_4H_9NO$, (XII), the molecules all lack a center of symmetry, crystallize in centrosymmetric space groups and have been observed to exhibit non-linear optical activity. In each case, the hydrazone skeleton is fairly planar, facilitated by the presence of two intramolecular hydrogen bonds and some partial N—N double-bond character. Each molecule is hydrogen bonded to one solvent molecule.

Comment

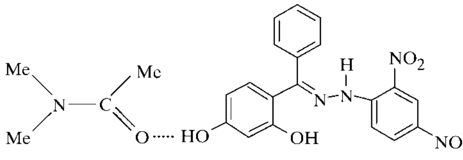
Hydrazone derivatives are an attractive class of non-linear optical (NLO) crystalline materials because of their large molecular non-linearities and their remarkable propensity to form non-centrosymmetric crystal systems (Serbutoviez *et al.*, 1995). The current approach to the development of practical NLO materials has focused on the use of a dihydroxy-functionalized hydrazone chromophore that can be easily synthesized and subsequently incorporated into a commercial epoxy polymer system. The preliminary goal was to provide for a systematic variation of the chromophore structure to study the resulting structure–property relationships. To this end, three hydrazones were synthesized by coupling 2,4-dinitrophenylhydrazine (2,4-DNPH) with three carbonyl compounds, namely, 2,4-dihydroxybenzaldehyde, 2,4-dihydroxyacetophenone and 2,4-dihydroxybenzophenone, to yield hydrazones (X), (XI) and (XII), respectively.



(X)



(XI)



(XII)

To confirm the structures of these three hydrazones, which are part of a series of related compounds currently under investigation [including compounds (I)–(IX), which are still in progress], the single-crystal data for these compounds are reported here. While each of the three compounds demonstrates NLO properties, it should be noted that each crystallizes in a centrosymmetric space group and that each molecule lacks a center of symmetry.

As seen in Figs. 1–3, all three compounds crystallize in a 1:1 ratio with solvent molecules [*N*,*N*-dimethylformamide (DMF) for (X) and (XI), and *N*,*N*-dimethylacetamide (DMAc) for (XII)], which accept a hydrogen bond at atom O7 from atom H1*A* of the *para*-hydroxy group of the hydrazone. In each case, across the C7═N1 bond, N2 is *E* to C4; simultaneously, each *R* substituent at C7 is *Z* to N2. In each molecule, two intramolecular hydrogen bonds, H2*A*···N1 and H2*B*···O3, help to facilitate the planarity of each hydrazone.

The 23-atom hydrazone skeleton [atoms O1–O6, N1–N4 and C1–C13, plus atom C14 for (XI) and (XII)] of (X) is the most planar of the three compounds, as it has an r.m.s. deviation of 0.061 Å, with atoms O2 and C5 having the largest deviations [0.137 (3) and 0.117 (3) Å, respectively] from the plane. On the other hand, (XI) and (XII) display some buckling. They have larger r.m.s. deviations (0.190 and 0.122 Å, respectively), in part due to atoms with larger deviations from the plane of the skeleton. For example, in (XI), atoms O2 and O6 have deviations of 0.488 (2) and 0.491 (2) Å, respectively, while in (XII), atoms O5 and C5 have deviations of 0.330 (3) and 0.180 (3) Å, respectively, from the 23-atom plane of the skeleton.

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In the case of compound (X), even the solvent molecule is coplanar with the plane of the hydrazone molecule; the r.m.s. deviation for all non-H atoms is 0.081 Å. However, neither solvent molecule in compounds (XI) and (XII) is coplanar with the hydrazone molecule (Figs. 2 and 3; Tables 3 and 5). The phenyl substituent (C14–C19) in compound (XII) is nearly perpendicular (Table 5) to the plane of the hydrazone skeleton, likely due in large part to steric problems around C7.

While the intramolecular hydrogen bonding minimizes the rotational freedom about the C4—C7 and N2—C8 bonds, rotation about N1—N2 is also reduced. The average of the C7═N1 bond lengths (Table 6) is ~3σ longer than the average of 13 C═N bond lengths (in PhC═NH coordination compounds) gleaned from the Cambridge Structural Database (CSD, Version 5.23; Allen, 2002). Similarly, the average of the N1—N2 bond lengths (Table 6) is ~20σ shorter than the average of five N—N bond lengths in hydrazine-solvated compounds in the CSD. This likely implies some N1—N2 double-bond character, thus reducing rotational mobility. The extent of this character changes as substituents vary on C7. The variation of C7═N1 bond lengths is 0.020 Å (~7σ), while that for N1—N2 is 0.015 Å (~5σ).

As seen in Table 6, some bond lengths near C7 are affected significantly ($\geq 3\sigma$) by changes in the *R* substituent on C7. Specifically, increases in bond lengths are noted for C7═N1, C4—C7 and C4⋯C5, concomitant with decreases in the N1—N2 and O2—C3 bond lengths as the *R* substituent changes from –H to –CH_3 to –Ph. The effect of going from H to alkyl to aromatic groups is felt as much as three bonds away from the C7—*R* bond.

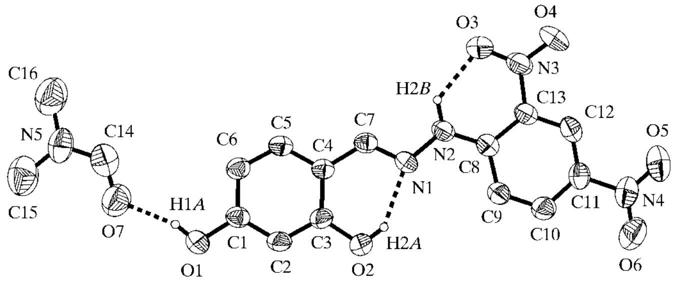

Figure 1
A view of the asymmetric unit of (X), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level, and significant H atoms are labeled and drawn as small spheres of arbitrary radii.

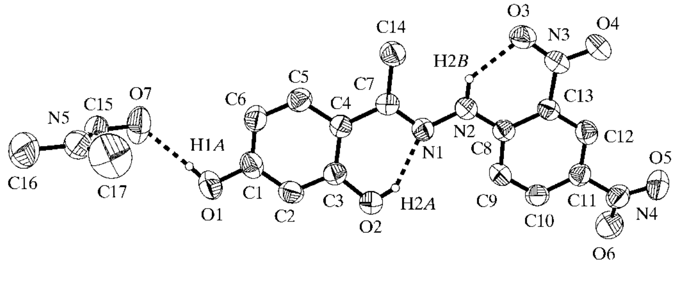

Figure 2
A view of the asymmetric unit of (XI), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level, and significant H atoms are labeled and drawn as small spheres of arbitrary radii.

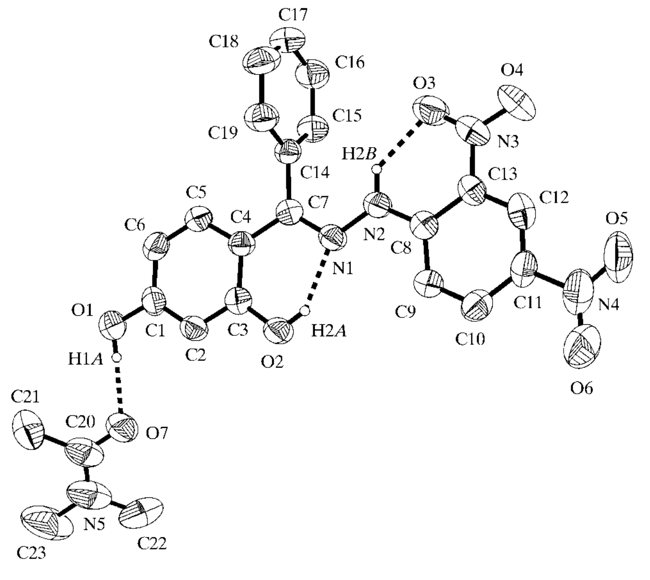

Figure 3
A view of the asymmetric unit of (XII), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level, and significant H atoms are labeled and drawn as small spheres of arbitrary radii.

Experimental

The three title hydrazones were synthesized according to a known procedure (Vogel, 1989) by mixing a solution of 2,4-DNPH in an ethanol–tetrahydrofuran solvent mixture [1:1 for (X), 3:1 for (XI), and 2:1 for (XII)] with the three dihydroxy–carbonyl compounds in a 1:1.05 molar ratio, with concentrated HCl as catalyst. The decomposition points (>523 K for each of the three hydrazones) were determined on a Thermal Analysis differential scanning calorimeter at a heating rate of 10 K min^{-1}. Crystals suitable for diffraction analysis were grown by slow evaporation of a saturated solution in DMF for hydrazones (X) and (XI), and in DMAc for hydrazone (XII). Each crystal was placed into a capillary and sealed with mother liquor.

Compound (X)

Crystal data

$C_{13}H_{10}N_4O_6\cdot C_3H_7NO$
M_r = 391.35
Monoclinic, $P2_1/c$
a = 19.697 (4) Å
b = 7.152 (1) Å
c = 12.949 (3) Å
β = 100.34 (2)°
V = 1794.5 (6) Å^3
Z = 4
D_x = 1.448 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 49 reflections
θ = 7.8–17.5°
μ = 0.12 mm^{-1}
T = 293 (2) K
Block cut from a larger crystal, red–orange
0.50 × 0.39 × 0.13 mm

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
3504 measured reflections
3119 independent reflections
1774 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\rm max} = 25.0^\circ$

$h = -23 \rightarrow 23$
$k = -8 \rightarrow 2$
$l = 0 \rightarrow 15$
3 standard reflections
every 50 reflections
intensity decay: 2.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.137$
$S = 1.01$
3110 reflections
258 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0059 (11)

Table 1
Hydrogen-bonding geometry (Å, °) for (X).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O7	0.82	1.83	2.626 (3)	163
O2—H2*A*···N1	0.82	1.97	2.691 (3)	146
N2—H2*B*···O3	0.86	1.96	2.603 (3)	131

Compound (XI)

Crystal data

$C_{14}H_{12}N_4O_6\cdot C_3H_7NO$
$M_r = 405.37$
Triclinic, $P\overline{1}$
$a = 7.928$ (1) Å
$b = 9.146$ (1) Å
$c = 14.362$ (2) Å
$\alpha = 104.45$ (1)°
$\beta = 91.04$ (1)°
$\gamma = 108.80$ (1)°
$V = 949.1$ (2) Å^3
$Z = 2$

$D_x = 1.418$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 9.6$–18.8°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Block cut from a larger crystal, red–orange
0.54 × 0.43 × 0.31 mm

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
4336 measured reflections
3310 independent reflections
2207 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.011$
$\theta_{\rm max} = 25.1^\circ$

$h = -3 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$
3 standard reflections
every 50 reflections
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.142$
$S = 1.01$
3298 reflections
268 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.1707P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.026 (4)

Table 2
Hydrogen-bonding geometry (Å, °) for (XI).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O7	0.82	1.86	2.677 (3)	175
O2—H2*A*···N1	0.82	1.88	2.590 (2)	146
N2—H2*B*···O3	0.86	1.94	2.590 (2)	131

Table 3
Selected r.m.s. deviations (Å) and dihedral angle (°) for (XI).

Plane 1	r.m.s. deviation	Plane 2	r.m.s. deviation	Angle
Hydrazone	0.194			
Hydrazone + C14	0.190	DMF	0.004	85.3 (1)

Compound (XII)

Crystal data

$C_{19}H_{14}N_4O_6\cdot C_4H_9NO$
$M_r = 481.46$
Triclinic, $P\overline{1}$
$a = 7.8155$ (9) Å
$b = 11.549$ (2) Å
$c = 13.904$ (2) Å
$\alpha = 100.38$ (1)°
$\beta = 95.80$ (1)°
$\gamma = 102.74$ (1)°
$V = 1191.0$ (3) Å^3

$Z = 2$
$D_x = 1.343$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 6.3$–20.7°
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, red–orange
0.50 × 0.38 × 0.38 mm

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
5472 measured reflections
4175 independent reflections
2517 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\rm max} = 25.1^\circ$

$h = -1 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections
every 50 reflections
intensity decay: 1.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.171$
$S = 1.04$
4153 reflections
322 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0921P)^2 + 0.1171P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.51$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.025 (4)

Table 4
Hydrogen-bonding geometry (Å, °) for (XII).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O7	0.82	1.82	2.630 (3)	172
O2—H2*A*···N1	0.82	1.90	2.623 (3)	146
N2—H2*B*···O3	0.86	1.95	2.600 (3)	131

Table 5
Selected r.m.s. deviations (Å) and dihedral angles (°) for (XII).

Plane 1	r.m.s. deviation	Plane 2	r.m.s. deviation	Angle
Hydrazone	0.109	C14–C19	0.002	84.04 (7)
Hydrazone	0.109	DMAc	0.031	44.7 (1)
Hydrazone + C14	0.122			

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Table 6
Selected interatomic distances (Å) for compounds (X)–(XII); the effects of changing *R* at C7 from –H to –CH_3 to –Ph.

Bond	(X)	(XI)	(XII)	Change†, Δ (Å)	Δ/s.u.$_{(X)}$‡	Range§, *R* (Å)	*R*/s.u.$_{(X)}$‡
O1—C1	1.358 (3)	1.358 (3)	1.352 (3)	−0.006	2.0	0.006	2.0
O2—C3	1.362 (3)	1.347 (3)	1.351 (3)	−0.009	3.0	0.015	5.0
C3⋯C4	1.408 (3)	1.415 (3)	1.414 (4)	0.006	2.0	0.007	2.3
C4⋯C5	1.386 (3)	1.397 (3)	1.396 (3)	0.010	3.3	0.011	3.7
C4—C7	1.439 (3)	1.469 (3)	1.462 (3)	0.023	7.7	0.030	10.0
C7—C14		1.496 (3)	1.502 (3)	0.006¶	2.0††	0.006	2.0
C7═N1	1.283 (3)	1.303 (3)	1.302 (3)	0.019	6.3	0.020	6.7
N1—N2	1.386 (3)	1.372 (2)	1.371 (3)	−0.015	5.0	0.015	5.0
N2—C8	1.343 (3)	1.354 (3)	1.348 (3)	0.005	1.7	0.011	3.7
N3—C13	1.447 (3)	1.450 (3)	1.447 (3)	−0.000	0.0	0.003	1.0
N4—C11	1.459 (4)	1.452 (3)	1.461 (4)	0.002	0.5	0.009	2.3

† Δ for (XII)−(X) ¶ Δ for (XII)−(XI) †† Δ/s.u.$_{(XI)}$ ‡ s.u.$_{(X)}$ is the s.u. in the bond length for (X) § Range = maximum value − minimum value.

In all three cases, the approximate positions of the two hydroxy H atoms were first obtained from a difference map. These atoms were then placed in 'ideal' positions and refined as a rotating group. Bond lengths were constrained (AFIX 43) at 0.93 Å for aromatic C—H, 0.96 Å (AFIX 137) for methyl C—H, 0.86 Å (AFIX 43) for N—H and 0.82 Å (AFIX 147) for O—H. $U_{\rm iso}$(H) values were fixed at $1.5U_{\rm eq}$ for OH and methyl H atoms, and $1.2U_{\rm eq}$ for all other H atoms. In the final stages of refinement for all three compounds, a few very small or negative F_o values were deemed to be in strong disagreement with their F_c values. The corresponding nine, 12, and 22 reflections for (X), (XI), and (XII), respectively, were eliminated from the final refinement. The percentage decay of the three standards was calculated as the average of their $\sigma(I)$ values.

For all three compounds, data collection: *P*3/*P*4-*PC Diffractometer Program* (Siemens, 1991); cell refinement: *P*3/*P*4-*PC Diffractometer Program*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXTL*/*PC* and *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1175). Services for accessing these data are described at the back of the journal.

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