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A combinatorial chemistry approach to new materials for non-linear optics. II.[1] 4-(Dimethylamino)cinnamaldehyde and a molecular complex of 4-methoxycinnamaldehyde with 2,4-dinitroaniline

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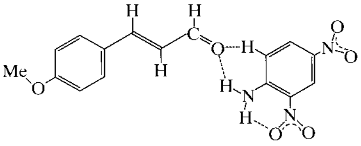
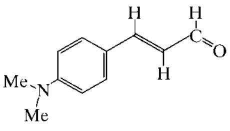
The combinatorial chemistry approach has been used to synthesize an array of Schiff bases. The structures of five of these Schiff bases have been confirmed by X-ray analysis [Nesterov, Timofeeva, Borbulevych, Antipin & Clark (2000). *Acta Cryst.* C**56**, 971–975]. In two cases, the reaction conditions were not sufficient to obtain the products in question. In one case, a molecular complex, $C_{10}H_{10}O_2\cdot C_6H_5N_3O_4$, of the starting products 4-methoxycinnamaldehyde and 2,4-dinitroaniline was found. X-ray analysis revealed hydrogen-bond formation between the molecules of these reagents in the crystal. In the other case, X-ray analysis demonstrated that no chemical reaction occurred under the reaction conditions, and only one starting reagent, 4-(dimethylamino)cinnamaldehyde, $C_{11}H_{13}NO$, was found in the precipitate.

Comment

In Part I of our communication (Nesterov *et al.*, 2000), we described the combinatorial reaction of aldehydes and amines to obtain a series of polar Schiff bases with non-linear optical properties. X-ray analysis was used to confirm the formulae and structures of the final products of the condensation reactions. It was shown that in most reactions the final products (Schiff bases) were obtained by a one-step reaction under the same conditions. In two cases, we were not able to obtain Schiff bases: in one case, we found a molecular complex, (4-*a*), of the starting reagents 4-methoxycinnamaldehyde, (*a*), and 2,4-dinitroaniline, (4), in the precipitate, and in the second case, one of the starting reagents, 4-(dimethylamino)cinnamaldehyde, (*b*), was found. The structure identification numbers of all the compounds mentioned in the present paper are in accordance with those used in Part I (Nesterov *et al.*, 2000). These results show that not all reagents belonging to the same starting groups of materials will give desirable final products under the same reaction conditions. Nevertheless, most of the expected Schiff bases were obtained (see Part I; Nesterov *et al.*, 2000), and most probably we would also be able to obtain the two Schiff bases in question, (4*a*) and (4*b*), by varying the reaction conditions.



(4-*a*)



(*b*)

The molecular structure of (4), which is part of the hydrogen-bonded complex (4-*a*) (Fig. 1), has been investigated several times, both as the compound itself (Prasad *et al.*, 1982), and as a clathrate with 1,4,7,10,13,16-hexaoxacyclooctadecane [(5); Weber & Sheldrick, 1981] and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane [(6); Watson *et al.*, 1988]. In all these crystals, the 2,4-dinitroaniline molecules have almost planar structures. The distances between the N atom of the amino group and the O atom of the nitro group in the *ortho* positions are 2.652 (2) in (4-*a*), 2.638 in (5), 2.657 in (6) and 2.621 Å in (4). These data, together with the planar molecular structure, indicate the presence of intramolecular hydrogen bonds in these molecules. Details of the geometry of the intramolecular hydrogen bonds in (4-*a*) are presented in Table 2.

Molecule (*a*) in (4-*a*) is also almost planar and shows no specific differences in comparison with the analogous derivative 4-nitrophenylcinnamaldehyde (Riassanen *et al.*, 1989). Molecules of the aldehyde, (*a*), and the amine, (4), are linked in the crystal of (4-*a*) by intermolecular hydrogen bonding (Table 2). The crystal of complex (4-*a*) consists of hydrogen-bonded dimers packed in layers; no other specific intermolecular contacts between dimers were found.

Molecule (*b*) also has an almost planar structure, with bond lengths and angles similar to the standard values. Molecules of (*b*) are packed in a head-to-tail manner, forming antiparallel chains.

In Part I (Nesterov *et al.*, 2000), the results of the successful syntheses of five Schiff bases were presented, showing that three nitroanilines, (1)–(3) (see Part I), give adducts with 4-methoxycinnamaldehyde, (*a*), or 4-(dimethylamino)cinnamaldehyde, (*b*). On the other hand, 2,4-dinitroaniline, (4), does not react with the two aldehydes mentioned above. Apparently, the lower reactivity of molecule (4) in comparison with molecules (1)–(3) under the same reaction conditions is due to the presence of an intramolecular hydrogen bond between the O atom of the nitro group and one of the H atoms of the amino group in the *ortho* position of (4). It is likely that redistribution of the electron density in the amino group makes the other H atom less active. In both the present and

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[1] Part I: Nesterov *et al.* (2000).

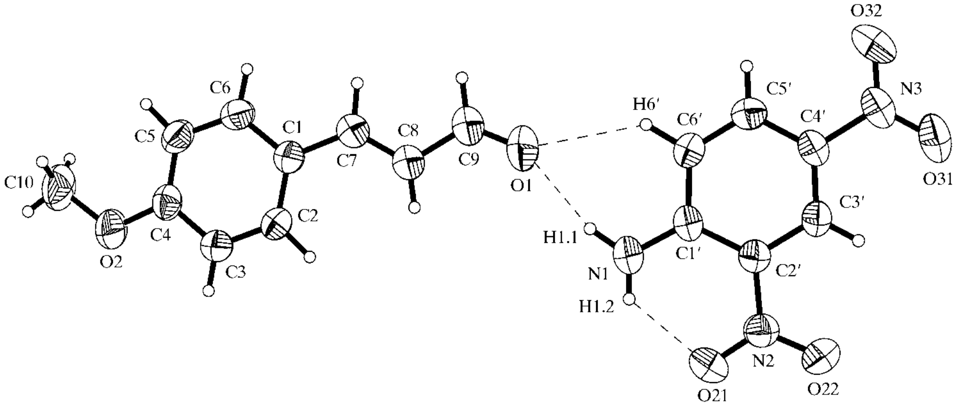

Figure 1
A molecular view of complex (4-*a*). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary small radii.

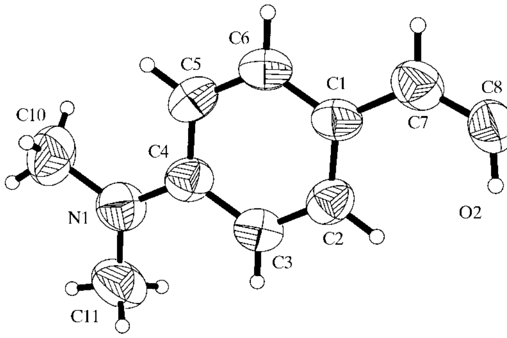

Figure 2
A molecular view of aldehyde (*b*). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary small radii.

the earlier paper, we have shown that combinatorial synthesis and X-ray characterization are a powerful combination.

Experimental

The molecular complex (4-*a*) was obtained by the reaction of (*a*) (0.005 mol) with (4) (0.005 mol) in the presence of a catalytic amount of acetic acid in ethanol (20 ml) under reflux for 1–3 min. The precipitate was separated from the solution (yield 61%, m.p. 366 K). Reaction of (4) with (*b*) under the same conditions gave one of the starting materials, (*b*), as a precipitate, as confirmed by its melting point of 408 K. In both cases, we used samples obtained from the reaction mixture for X-ray investigation. Crystals of (*b*) were thin and of poor quality; recrystallization gave no improvement in their quality.

Compound (4-*a*)

Crystal data

$C_{10}H_{10}O_2 \cdot C_6H_5N_3O_4$
$M_r = 345.31$
Triclinic, $P\overline{1}$
$a = 7.3490$ (15) Å
$b = 9.2520$ (19) Å
$c = 12.523$ (3) Å
$\alpha = 108.01$ (3)°
$\beta = 93.48$ (3)°
$\gamma = 94.40$ (3)°
$V = 804.2$ (3) Å^3
$Z = 2$
$D_x = 1.426$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11$–$12°$
$\mu = 0.111$ mm^{-1}
$T = 298$ (2) K
Parallelepipedic prism, yellow
0.50 × 0.35 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
4088 measured reflections
3786 independent reflections
2370 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 27.96°$
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$
3 standard reflections every 97 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.156$
$S = 1.023$
3786 reflections
286 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.152P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (4-*a*).

O1—C9	1.204 (3)	O31—N3	1.221 (2)
C1—C7	1.445 (3)	O32—N3	1.225 (2)
C7—C8	1.326 (3)	N1—C1′	1.333 (2)
C8—C9	1.435 (3)	N2—C2′	1.443 (2)
O21—N2	1.227 (2)	N3—C4′	1.456 (2)
O22—N2	1.231 (2)	C1′—C2′	1.424 (2)
C8—C7—C1	129.6 (2)	O22—N2—C2′	118.24 (15)
C7—C8—C9	120.3 (2)	O31—N3—O32	122.96 (17)
O1—C9—C8	127.2 (2)	O31—N3—C4′	118.96 (18)
O21—N2—O22	122.24 (16)	O32—N3—C4′	118.08 (17)
O21—N2—C2′	119.52 (15)		
C10—O2—C4—C3	178.6 (2)	O21—N2—C2′—C1′	1.7 (3)
C2—C1—C7—C8	−3.6 (4)	O22—N2—C2′—C1′	−177.70 (16)
C1—C7—C8—C9	−179.7 (2)	O31—N3—C4′—C3′	3.0 (3)
C7—C8—C9—O1	177.6 (3)	O32—N3—C4′—C3′	−177.58 (18)

Table 2
Hydrogen-bonding geometry (Å, °) for (4-*a*).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1.2···O21	0.85 (3)	2.02 (2)	2.652 (2)	130 (1)
N1—H1.1···O1	0.91 (3)	2.09 (3)	2.978 (2)	164 (1)
C6′—H6′···O1	0.98 (2)	2.51 (2)	3.308 (2)	138 (1)

Compound (*b*)

Crystal data

$C_{11}H_{13}NO$
$M_r = 175.22$
Orthorhombic, *Pbca*
$a = 10.040\ (6)$ Å
$b = 7.733\ (3)$ Å
$c = 25.620\ (13)$ Å
$V = 1989.1\ (17)$ Å^3
$Z = 8$
$D_x = 1.170$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–$11°$
$\mu = 0.075$ mm^{-1}
$T = 298\ (2)$ K
Plate, light green
0.5 × 0.4 × 0.1 mm

Data collection

Siemens *P*3/*PC* diffractometer
$\theta/2\theta$ scans
1755 measured reflections
1755 independent reflections
1070 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.05°$

$h = 0 \rightarrow 11$
$k = 0 \rightarrow 9$
$l = -30 \rightarrow 0$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.123$
$wR(F^2) = 0.257$
$S = 1.141$
1755 reflections
120 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 5.11P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.014$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (*b*).

O1—C9	1.204 (8)	C7—C8	1.320 (7)
N1—C4	1.374 (6)	C8—C9	1.430 (8)
C1—C7	1.466 (7)		
C8—C7—C1	129.3 (6)	O1—C9—C8	126.3 (8)
C7—C8—C9	121.2 (6)		
C2—C1—C7—C8	−9.6 (9)	C7—C8—C9—O1	175.5 (7)
C1—C7—C8—C9	−175.5 (6)		

For the molecular complex (4-*a*), all H atoms were freely refined [C—H range 0.93 (2)–1.00 (2) Å].

For complex (4-*a*), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*. For compound (*b*), data collection: *P*3/*PC Diffractometer Program* (Siemens, 1989); cell refinement: *P*3/*PC Diffractometer Program*. For both compounds, data reduction: *SHELXTL-Plus* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1394). Services for accessing these data are described at the back of the journal.

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