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A combinatorial chemistry approach to new materials for non-linear optics. I. Five Schiff bases

Vladimir N. Nesterov,[a]* Tatiana V. Timofeeva,[a] Oleg Ya. Borbulevych,[a] Mikhail Yu. Antipin[a,b] and Ronald D. Clark[a]

[a]Department of Physical Sciences, New Mexico Highlands University, Las Vegas, NM 87701, USA, and [b]Institute of Organoelement Compounds of the Russian Academy of Sciences, 28 Vavilov St., Moscow, Russian Federation
Correspondence e-mail: vlad@kremlin.nmhu.edu

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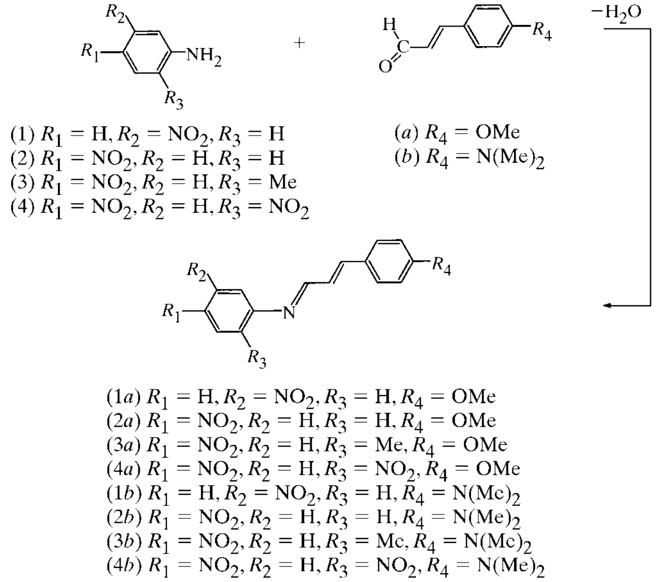
A combinatorial chemistry approach has been used to synthesize an array of Schiff bases, five of which, namely *N*-[(*E*,2*E*)-3-(4-methoxyphenyl)-2-propenylidene]-3-nitroaniline, $C_{16}H_{14}N_2O_3$, (1*a*), *N*-[(*E*,2*E*)-3-(4-methoxyphenyl)-2-propenylidene]-4-nitroaniline, $C_{16}H_{14}N_2O_3$, (2*a*), *N*-{(*E*,2*E*)-3-[4-(dimethylamino)phenyl]-2-propenylidene}-3-nitroaniline, $C_{17}H_{17}N_3O_2$, (1*b*), *N*-{(*E*,2*E*)-3-[4-(dimethylamino)phenyl]-2-propenylidene}-4-nitroaniline, $C_{17}H_{17}N_3O_2$, (2*b*), and *N*-{(*E*,2*E*)-3-[4-(dimethylamino)phenyl]-2-propenylidene}-2-methyl-4-nitroaniline, $C_{18}H_{19}N_3O_2$, (3*b*), have been structurally characterized. A stack structure is observed for (1*a*) and (1*b*) in the crystal phase. Experimental and calculated molecular structures are discussed for these compounds which belong to a chemical class having potential applications as non-linear optical materials.

Comment

Combinatorial chemistry is a new field of synthetic chemistry which leads to fast synthesis of a wide variety (libraries) of products for particular applications. The recent success of combinatorial methods in the field of drug discovery (Tarby *et al.*, 1996) has triggered exploration in the field of materials such as inorganic luminescent materials and catalysts (Danielson *et al.*, 1997; Shimizu *et al.*, 1997).

There are two approaches in combinatorial synthesis which lead to either diverse or focused combinatorial libraries. Recently, we started an investigation of the combinatorial synthesis procedure for the rapid formation of large libraries of polar compounds (a focused library) which can be used for preparation of non-linear optical (NLO) materials (Zyss *et al.*, 1994). We performed quantum chemical evaluations of the first-order molecular hyperpolarizabilities (β) of the compounds in question before undertaking the synthesis of a small combinatorial library. Since the crystal structure is a very important characteristic of such materials, we performed X-ray analyses of the products in all cases where we were able to obtain suitable single crystals. To our knowledge, this study represents the first systematic application of chemical crystallography to the investigation of an array of combinatorial products. For the targeted library, we used amines (1–4) and aldehydes (*a*, *b*) as the building blocks and we assumed that we would be able to synthesize eight polar Schiff bases by condensation reactions (scheme).



(1) $R_1 = H, R_2 = NO_2, R_3 = H$
(2) $R_1 = NO_2, R_2 = H, R_3 = H$
(3) $R_1 = NO_2, R_2 = H, R_3 = Me$
(4) $R_1 = NO_2, R_2 = H, R_3 = NO_2$

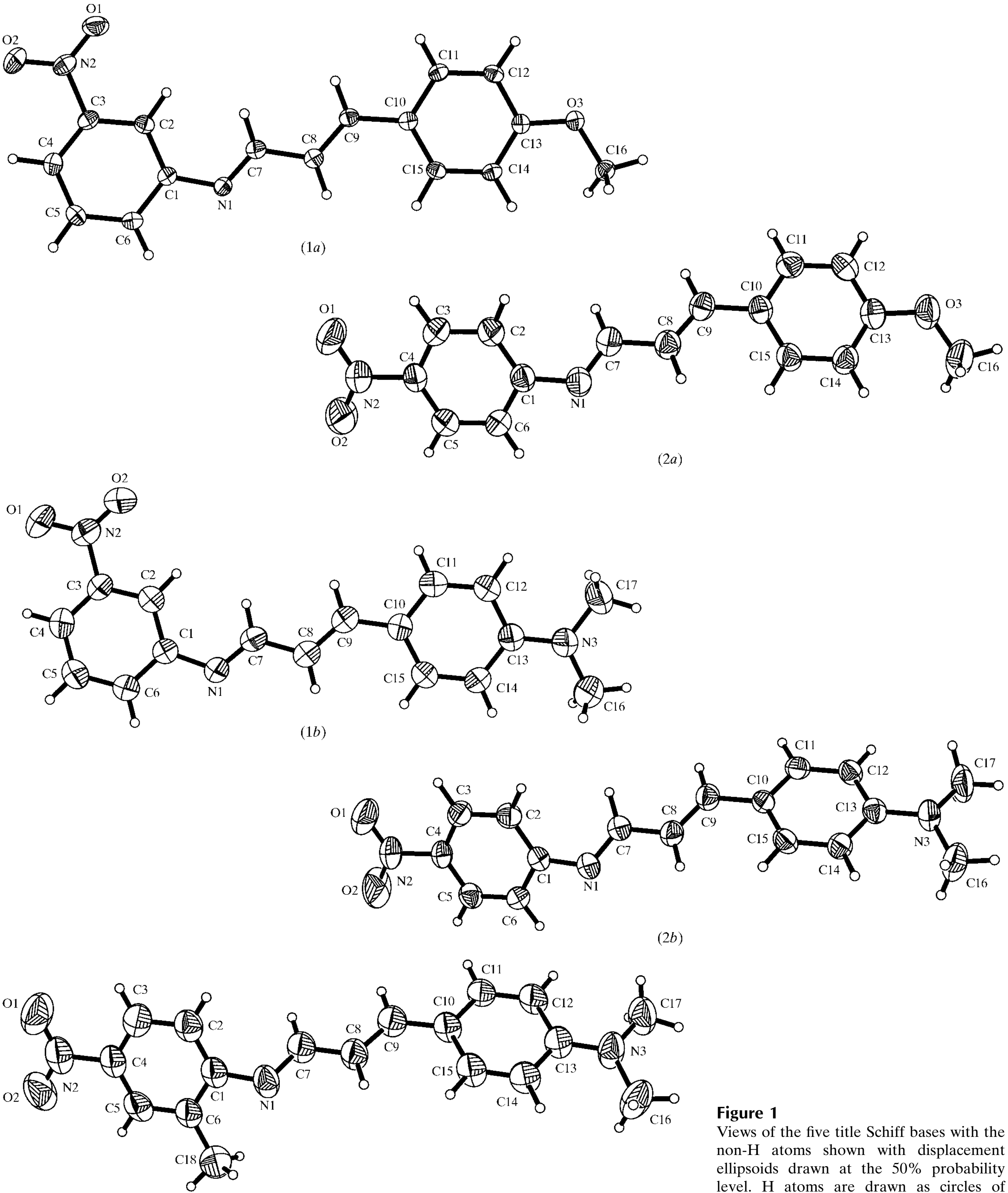
(*a*) $R_4 = OMe$
(*b*) $R_4 = N(Me)_2$

(1*a*) $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = OMe$
(2*a*) $R_1 = NO_2, R_2 = H, R_3 = H, R_4 = OMe$
(3*a*) $R_1 = NO_2, R_2 = H, R_3 = Me, R_4 = OMe$
(4*a*) $R_1 = NO_2, R_2 = H, R_3 = NO_2, R_4 = OMe$
(1*b*) $R_1 = H, R_2 = NO_2, R_3 = H, R_4 = N(Me)_2$
(2*b*) $R_1 = NO_2, R_2 = H, R_3 = H, R_4 = N(Me)_2$
(3*b*) $R_1 = NO_2, R_2 = H, R_3 = Me, R_4 = N(Me)_2$
(4*b*) $R_1 = NO_2, R_2 = H, R_3 = NO_2, R_4 = N(Me)_2$

Because of the structural characteristics of the Schiff base products (*i.e.* electron donor and acceptor groups connected to a π-conjugated chain), they will have potential as NLO or electro-optical materials. Quantum chemical calculations of average molecular hyperpolarizabilities (β) support this conclusion. It can be seen from Table 2 that the β values increase in the series (1) → (4) and (*a*) → (*b*), in agreement with the activity of donor and acceptor groups in these compounds.

In each case, the color of the product in comparison with that of the starting material indicated that the expected chemical reaction had taken place. In all cases, we also observed precipitation of crystalline products. We were able to obtain suitable single crystals for all products except for (3*a*), where the crystals were too small. The results of structure investigations indicated that the conditions we used for the condensation reactions were not favorable for obtaining the Schiff base for adducts (4*a*) and (4*b*). From the first of these reactions, a molecular complex (4-*a*) was observed while, in the second, one of the starting materials (*b*) was identified. The structures of these two compounds are described in a following paper (Nesterov *et al.*, 2000).

Bond-length alternation is observed in the central π-conjugated chain of all five molecules (1*a*), (2*a*), (1*b*), (2*b*) and (3*b*) (see Fig. 1, respectively, and Table 1). Similar alternations were found previously in Schiff bases with different substituents (Cl, Br or Me) on one of the phenyl rings (Karaev & Furmanova, 1984; Childs *et al.*, 1989; Ercan *et al.*, 1996). The C1—N1, N1═C7 and C8—C9 bond lengths in the chains are similar both in the five molecules studied here (Table 1) and in four analogous molecules (Karaev & Furmanova, 1984; Childs *et al.*, 1989; Ercan *et al.*, 1996). In contrast, the C7—C8 and C9—C10 distances in (1*b*) and (3*b*) are considerably shorter than those observed in all other compounds. It should be noted that phenyl rings with a dimethylamino substituent, as seen in (1*b*) and (3*b*), exhibit noticeable quinoid character



(1*a*)

(2*a*)

(1*b*)

(2*b*)

(3*b*)

Figure 1
Views of the five title Schiff bases with the non-H atoms shown with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary small radii for clarity.

demonstrated by the shortening of the C11—C12 and C14—C15 bond lengths (Table 1) compared to the standard C$\cdots$C distance of 1.398 Å (Allen *et al.*, 1987). The shortening of these bonds is less pronounced in (1*a*), (2*a*) and (2*b*). Other phenyl-ring bond lengths lie close to that of the standard C$\cdots$C bond. The quinoid character of the phenyl ring is actually rather typical for rings bearing electron donor and acceptor substituents in *para* positions (Domenicano, 1992), and this feature is considered important in potential NLO compounds (Zyss & Chemla, 1987).

Molecules of (2*a*), (2*b*) and (3*b*) (Fig. 1) are non-planar due to rotation of both phenyl rings with respect to the central planar molecular fragment, but the rotation of the nitrophenyl ring is consistently greater than that of the other aromatic ring: *AM*1 calculations (Dewar *et al.*, 1985) reproduce the features of the non-planarity in these molecules very well (Table 1). A parallel observation was made for related compounds where rotations of the aniline rings were about 40° (Karaev & Furmanova, 1984; Childs *et al.*, 1989; Ercan *et al.*, 1996).

In contrast, molecules of (1*b*) (Fig. 1) are almost planar in the solid state (Table 1). Since *AM*1 calculations predict non-planarity of this molecule (Table 1), the influence of crystal-packing forces might be invoked to explain the discrepancy between experimental and theoretical results. Indeed, molecules are stacked along [100] with a separation of only 3.31 (1) Å between the least-squares mean planes of neighboring molecules. In addition, similar packing but in the direction [010] is observed in the crystal of (1*a*). Consequently, molecule (1*a*) is closer to planarity than (2*a*), (2*b*) and (3*b*) (Table 1). Significantly, such stacking is absent in the structures of (2*a*), (2*b*) and (3*b*).

Our results show the potential use of combinatorial synthesis for obtaining targeted libraries in materials chemistry. Although, in this case, six Schiff base compounds from a small array of eight possible products were synthesized, all five which were the subject of successful structure determination were found to crystallize in centrosymmetric space groups. Since in centrosymmetric crystals the superposition of inverted tensors of the third rank which describe molecular hyperpolarizability (β) is equal to zero, such crystals do not generate second harmonics (Zyss & Chemla, 1987). This precludes the application of bulk crystals or crystalline films of the compounds studied as NLO materials. On the other hand, the centrosymmetric patterns might be easily destroyed by introducing these compounds into polymer matrices doped by an active NLO chromophore (Agullo-Lopez *et al.*, 1994). Thus, the title compounds might be utilized as active dopants in polymer-based second harmonic generating, electrooptic or photorefractive materials.

Experimental

All Schiff bases were obtained by the reaction of 4-methoxycinnamaldehyde, (*a*), or 4-dimethylaminocinnamaldehyde, (*b*) (0.005 mol), with amines (1)–(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 precipitates were isolated and recrystallized from ethanol (30 ml) in the presence of a small amount of acetic acid. Yields: (1*a*) 78, (1*b*) 74, (2*a*) 85, (2*b*) 82, (3*a*) 78 and (3*b*) 70%. Crystals were obtained by isothermal evaporation from CH_3CN solutions. UV/vis (λ_{max}/nm, acetone solution): 381 (1*a*), 413 (1*b*), 365 (2*a*), 444 (2*b*), 355 (3*a*) and 431 (3*b*).

Compound (1*a*)

Crystal data

$C_{16}H_{14}N_2O_3$
$M_r = 282.29$
Monoclinic, $P2_1/n$
$a = 15.7883\ (8)$ Å
$b = 3.9239\ (2)$ Å
$c = 22.6063\ (11)$ Å
$\beta = 105.7670\ (10)^\circ$
$V = 1347.80\ (12)$ Å^3
$Z = 4$
$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5200 reflections
$\theta = 2$–24°
$\mu = 0.098$ mm^{-1}
$T = 100\ (2)$ K
Square prism, yellow
0.3 × 0.1 × 0.1 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
14 296 measured reflections
3938 independent reflections
2603 reflections with $I > 2\sigma(I)$
$R_{int} = 0.063$
$\theta_{max} = 30.03^\circ$
$h = -22 \rightarrow 20$
$k = -5 \rightarrow 5$
$l = -31 \rightarrow 31$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.126$
$S = 1.024$
3925 reflections
246 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0889P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Compound (2*a*)

Crystal data

$C_{16}H_{14}N_2O_3$
$M_r = 282.29$
Orthorhombic, $Pbca$
$a = 10.413\ (2)$ Å
$b = 7.5990\ (15)$ Å
$c = 36.010\ (7)$ Å
$V = 2849.4\ (10)$ Å^3
$Z = 8$
$D_x = 1.316$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–11°
$\mu = 0.092$ mm^{-1}
$T = 298\ (2)$ K
Plate, yellow
0.60 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
3579 measured reflections
3400 independent reflections
1593 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 27.98^\circ$
$h = -13 \rightarrow 0$
$k = -10 \rightarrow 0$
$l = 0 \rightarrow 47$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.106$
$S = 1.159$
3346 reflections
247 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 1.1439P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXTL-Plus* (Sheldrick, 1994)
Extinction coefficient: 0.0137 (14)

Compound (1*b*)

Crystal data

$C_{17}H_{17}N_3O_2$
$M_r = 295.34$
Triclinic, $P\bar{1}$
$a = 6.7910$ (14) Å
$b = 10.204$ (2) Å
$c = 12.185$ (2) Å
$\alpha = 113.20$ (3)°
$\beta = 98.97$ (3)°
$\gamma = 95.53$ (3)°
$V = 754.9$ (3) Å^3
$Z = 2$
$D_x = 1.299$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–11°
$\mu = 0.087$ mm^{-1}
$T = 295$ (2) K
Plate, yellow
0.60 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
2899 measured reflections
2650 independent reflections
1255 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\max} = 24.98°$
$h = 0 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.094$
$S = 1.135$
2595 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.11$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}

Compound (2*b*)

Crystal data

$C_{17}H_{17}N_3O_2$
$M_r = 295.34$
Triclinic, $P\bar{1}$
$a = 6.1650$ (12) Å
$b = 7.2730$ (15) Å
$c = 17.158$ (3) Å
$\alpha = 90.70$ (3)°
$\beta = 100.10$ (3)°
$\gamma = 91.37$ (3)°
$V = 757.1$ (3) Å^3
$Z = 2$
$D_x = 1.296$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–11°
$\mu = 0.087$ mm^{-1}
$T = 298$ (2) K
Square prism, dark yellow
0.40 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
4620 measured reflections
4007 independent reflections
1534 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 28.96°$
$h = 0 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -23 \rightarrow 23$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.107$
$S = 1.224$
3955 reflections
267 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Compound (3*b*)

Crystal data

$C_{18}H_{19}N_3O_2$
$M_r = 309.36$
Triclinic, $P\bar{1}$
$a = 8.438$ (2) Å
$b = 9.609$ (2) Å
$c = 10.546$ (2) Å
$\alpha = 72.95$ (3)°
$\beta = 86.13$ (3)°
$\gamma = 89.81$ (3)°
$V = 815.5$ (3) Å^3
$Z = 2$
$D_x = 1.260$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–11°
$\mu = 0.084$ mm^{-1}
$T = 295$ (2) K
Plate, yellow
0.40 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
3073 measured reflections
2858 independent reflections
1393 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.086$
$\theta_{\max} = 24.97°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.080$
$wR(F^2) = 0.201$
$S = 1.143$
2779 reflections
211 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1556P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Comparison of geometric parameters and characteristics of planarity (Å, °) for molecules (1*a*), (2*a*), (1*b*), (2*b*) and (3*b*).

Parameter	(1*a*)	(2*a*)	(1*b*)	(2*b*)	(3*b*)
N1—C7	1.286 (2)	1.266 (3)	1.261 (2)	1.274 (3)	1.281 (4)
N1—C1	1.409 (2)	1.411 (3)	1.413 (2)	1.409 (3)	1.404 (4)
C7—C8	1.441 (2)	1.450 (3)	1.423 (3)	1.439 (4)	1.415 (5)
C8—C9	1.348 (2)	1.328 (3)	1.337 (3)	1.333 (4)	1.336 (5)
C9—C10	1.459 (2)	1.462 (3)	1.429 (3)	1.459 (3)	1.439 (5)
C10—C11	1.405 (2)	1.391 (3)	1.396 (3)	1.394 (3)	1.390 (5)
C11—C12	1.376 (2)	1.370 (3)	1.366 (3)	1.375 (3)	1.354 (5)
C12—C13	1.401 (2)	1.379 (3)	1.397 (3)	1.401 (3)	1.422 (5)
C13—C14	1.394 (2)	1.384 (3)	1.404 (3)	1.408 (3)	1.398 (5)
C14—C15	1.389 (2)	1.378 (3)	1.366 (3)	1.370 (4)	1.352 (5)
C10—C15	1.400 (2)	1.386 (3)	1.394 (3)	1.392 (3)	1.409 (5)
C7—N1—C1—C2†	23.5 (2)	−40.2 (4)	4.9 (3)	−37.3 (4)	−47.6 (5)
C7—N1—C1—C2‡	29.1	−38.6	30.6	−36.3	−41.5
C8—C9—C10—C15†	−14.2 (2)	7.7 (4)	4.0 (4)	−16.0 (4)	−4.1 (6)
C8—C9—C10—C15‡	−19.5	10.0	−14.1	−15.3	0.7
R.m.s. deviation§	0.1000	0.285	0.076	0.437	0.382
Maximum deviation¶	0.214 (1)	−0.548 (3)	0.135 (2)	0.700 (2)	−0.647 (3)

† According to X-ray data. ‡ According to *AM*1 calculations. § For non-H atoms and excluding substituents ($-NO_2$, $-CH_3$, $-NMe_2$). ¶ Maximum deviation from the molecular plane is observed for N1 in (1*a*) and for C5 in the other compounds.

Table 2
Calculated values of β (10^{-51} C m^3 V^{-2}) for compounds (1*a*)–(4*b*).

	(1*a*)	(2*a*)	(3*a*)	(4*a*)	(1*b*)	(2*b*)	(3*b*)	(4*b*)
β	77 (1)	107 (6)	101 (6)	143 (6)	134 (4)	173 (11)	172 (11)	217 (19)

The molecular structures of (1*a*)–(4*b*) were calculated by the *AM*1 semi-empirical quantum-chemical method (Dewar *et al.*, 1985) with full geometry optimization using the *GAMESS* program (Schmidt *et al.*, 1993). Calculations of average molecular hyperpolarizabilities (β in 10^{-51} C m^3 V^{-2}) were carried out with the finite field approach using modified *MOPAC* (*AM*1) and *HYPER* programs (Cardelino *et al.*, 1991, 1997).

In (1*a*), (2*a*) and (2*b*), H atoms were located from ΔF syntheses and thereafter refined freely. For the remaining structures, (1*b*) and (3*b*), methyl-H atoms were located in a ΔF synthesis and thereafter refined as part of a rigid rotating group, while others were placed in geometrically calculated positions and refined using a riding model.

For the five compounds (1*a*), (1*b*), (2*a*), (2*b*) and (3*b*), the respective total number of reflections suppressed with $I < 2\sigma(I)$ was 13, 55, 47, 52 and 79; the corresponding number suppressed due to systematic errors was 11, 30, 32 28 and 62.

For compound (1*a*), data collection and cell refinement: *SMART* (Siemens, 1994); for all other compounds, data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989); for compound (1*a*), data reduction: *SHELXTL-Plus* (Sheldrick, 1994); for all other compounds, data reduction: *PROFIT* (Streltsov & Zavodnik, 1989). For compound (1*a*), program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); for all other compounds, program(s) used to solve structure: *SHELXTL-Plus*; for compound (1*a*), program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); for all other compounds, program(s) used to refine structure: *SHELXTL-Plus*; for all compounds, molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1393). Services for accessing these data are described at the back of the journal.

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