

# Chiral Pyrrolo[1,2-*a*]quinolines as Second-Order Nonlinear Optical Materials

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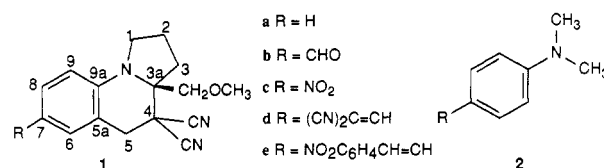
The synthesis and nonlinear optical properties of a series of chiral pyrrolo[1,2-*a*]quinolines **1a-e** is presented. The microscopic hyperpolarizabilities ( $\beta_z$ ) were determined by EFISH measurements and the macroscopic susceptibilities ( $\chi^2$ ) were estimated by the Kurtz powder test. A small fixed angle of the annelated pyrrolidine donor unit with respect to the aromatic  $\pi$ -system renders the whole donor- $\pi$ -acceptor system chiral. The small deviation from planarity of approximately  $10 \pm 3^\circ$  causes no observable reduction of the microscopic  $\beta_z$  value in comparison with the planar conjugated *N,N*-dimethylaniline analogues. The powder test showed phase matching for all pyrrolo[1,2-*a*]quinolines with an electron-withdrawing substituent at C-7 (**1b-e**). The aldehyde **1b** crystallizes in the  $P2_12_12_1$  space group and was calculated to have an efficiency of 8.3% of  $\beta$  under optimal phasematch conditions. The nitro derivative **1c** crystallizes in the favorable space group  $P2_1$  ( $Z = 2$ ) in which the angles of the two independent molecules with the optical *b* axis are  $71.7^\circ$  and  $43.5^\circ$ .

## Introduction

Organic molecules with strong electron-donating and -withdrawing substituents interconnected by a long  $\pi$ -system (D- $\pi$ -A molecules) have promising properties for nonlinear optical materials.<sup>1,2</sup> For the observation of second-order nonlinear optical (NLO) phenomena, i.e., frequency doubling of laser light or electrooptic phase modulation, a noncentrosymmetric orientation of the molecules in the material is necessary. One of the methods to achieve such a noncentrosymmetric orientation is to pole the molecules with their permanent dipole moment in a polymeric matrix with the aid of a strong electric field. However, the NLO-active lifetime of these polymers is limited because of the relaxation of the oriented molecules. Another approach to obtain noncentrosymmetric NLO materials is the preparation of multilayers by the Langmuir-Blodgett technique. Unfortunately, until now it has not been possible to obtain stable films of more than 300 NLO-active layers.<sup>3-5</sup> A third possibility to obtain NLO-active material is the use of crystals of chiral molecules that crystallize a priori in a noncentrosymmetric way. The chiral center in molecules investigated thus far, such as *N*-(4-nitrophenyl)-(S)-prolinol (NPP) and 2,4-dinitrophenyl-(L)-alanine methyl ester (MAP), is attached in a side chain of the molecule. In principle, however, the D- $\pi$ -A part of such optically active molecules is still able to orientate in a centrosymmetric way.<sup>1,2</sup>

In this paper we present a class of optically active molecules, viz., the pyrrolo[1,2-*a*]quinolines, in which the D- $\pi$ -A system is inherently chiral in addition to an asymmetric C atom. In the rigid annelated tricyclic system the pyrrolidine ring is forced slightly out of plane. This nonplanarity with respect to the aromatic ring renders the whole D- $\pi$ -A system chiral. Only one of the enantiomeric D- $\pi$ -A systems is formed in the synthesis of **1a**<sup>6,7</sup> due to asymmetric induction of the chiral C atom in the pyrrolidine ring.

Chart I



To establish the molecular NLO properties of the molecules, microscopic hyperpolarizabilities ( $\beta_z$ ) were determined by electric-field-induced second harmonic generation (EFISH) measurements.<sup>8</sup> The macroscopic susceptibilities ( $\chi^2$ ) were estimated by the Kurtz powder test.<sup>9</sup> For **1b** (R = CHO) and **1c** (R = NO<sub>2</sub>) the crystallographic data were obtained by single-crystal X-ray analysis.

## Results and Discussion

**Synthesis.** The synthesis of chiral pyrrolo[1,2-*a*]quinolines has been investigated in detail by our group.<sup>6,7</sup> A general synthesis is outlined in Scheme I. The cyclization reaction in the last step occurs with retention of the chirality at the bridgehead carbon atom C-3a, and there-

(1) Williams, D. J. *Angew. Chem.* 1984, 96, 637.

(2) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, 1987; Vols. 1 and 2.

(3) Ashwell, A. J.; Dawnay, E. J. C.; Kuczynski, A. P. *J. Chem. Soc., Chem. Commun.* 1990, 1355.

(4) Ashwell, A. J.; Dawnay, E. J. C.; Kuczynski, A. P.; Martin, P. J. *Proc. SPIE* 1990, 1361, 589.

(5) Decher, G.; Tieke, B.; Bosshard, C.; Günter, P. *J. Chem. Soc., Chem. Commun.* 1988, 933.

(6) (a) Nijhuis, W. H. N.; Verboom, W.; Abu El-Fadl, A.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* 1989, 54, 199. (b) Nijhuis, W. H. N.; Verboom, W.; Abu El-Fadl, A.; van Hummel, G. J.; Reinhoudt, D. N. *J. Org. Chem.* 1989, 54, 209.

(7) Kelderman, E.; Noorlander-Bunt, H. G.; van Eerden, J.; Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* 1991, 110, 115.

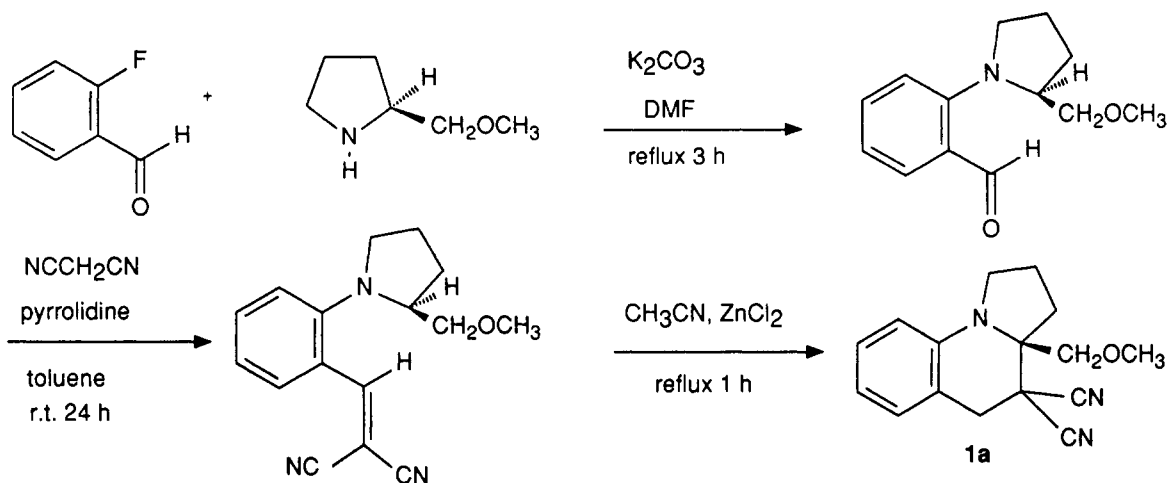
(8) Derhaeg, L.; Samyn, C.; Persoons, A. In *Organic Molecules for Nonlinear Optics and Photonics*; Messier, J., et al., Eds.; Kluwer Academic Publishers: The Netherlands, 1991; p 177.

(9) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* 1968, 39, 3798.

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Scheme I. Synthesis of the Chiral Pyrrolo[1,2-a]quinoline 1a<sup>a</sup><sup>a</sup> r.t. = room temperature.Table I. Microscopic Nonlinear Optical Data of 7-Substituted Pyrrolo[1,2-a]quinolines 1a-e and the Corresponding Values<sup>11,12</sup> for the *N,N*-Dimethylanilines 2a-e

subst	$\mu$ , D		$\beta_z(1064 \text{ nm})^{a,b}$		$\beta_z(1910 \text{ nm})^a$		$\lambda_{\text{max}}^b$ , nm	
	1	2 <sup>c</sup>	1	2	1	2 <sup>d</sup>	1	2
a	3.4	1.6	1.7		1.2	(1.1) <sup>e</sup>	306	298
b	4.3	5.6	17		11	(6.3) <sup>f</sup>	331	326
c	4.7	6.9	47		26	(12) <sup>g</sup>	373	376
d	7.6	8.4	84	119	35	46 (22) <sup>h</sup>	418	430
e	6.3	7.4	326		137	(83) <sup>b</sup>	417	424

<sup>a</sup> In  $10^{-30}$  esu  $\pm 20\%$ . <sup>b</sup> In chloroform. <sup>c</sup> Dipole moments taken from ref 12 except for 2d, which has been determined in this work. <sup>d</sup> Value between brackets measured by Cheng et al.<sup>11</sup> <sup>e</sup> Neat. <sup>f</sup> In *p*-dioxane. <sup>g</sup> In acetone. <sup>h</sup> In dichloromethane. Donor is julolidine instead of *N,N*-dimethylaniline.

fore one enantiomer is formed. The chirality at this C-3a atom is comparable with the type of chirality in the side chain of NPP and MAP. An additional factor in these pyrrolo[1,2-a]quinolines is that upon ring closure 1a is formed as a right handed turn when starting from (S)-2-(methoxymethyl)pyrrolidine; this renders the entire D- $\pi$ -A system chiral (see Scheme I).

The introduction of different acceptor groups in the  $\pi$ -system can be achieved with high selectivity at the 7-position (Chart I). The aldehyde 1b and the nitro-substituted 1c were obtained by an electrophilic aromatic substitution of 1a. The dicyanovinyl (1d) and the 4-nitrostilbene (1e) derivatives were synthesized by a condensation reaction of 1b with malononitrile and 4-nitrobenzyl phosphonate, respectively. Since the compounds 1a-e have an inherently chiral D- $\pi$ -A system, they may be interesting candidates for use in second-order NLO.

In a previous paper we described the macroscopic nonlinear optical properties of crystals of the 5-methyl derivative of 1a and found that this material shows phase-matching ability of the generated second harmonic radiation.<sup>10</sup>

**EFISH Measurements.** For the determination of the microscopic nonlinear optical properties of 1a-e and 2d as a reference material for literature comparison, EFISH measurements were performed to obtain  $\mu\beta_z$ . The dipole moments  $\mu$  were derived from measurements of the dielectric constant using a capacitance bridge. This allows the calculation of the hyperpolarizability  $\beta_z$ .<sup>8</sup> To compare our data with  $\beta_z$  values of para-substituted *N,N*-dimethylaniline analogues 2a-e, given in the literature,<sup>11</sup> the

$\beta_z$  values at 1064 nm were converted to  $\beta_z$  values at 1910 nm, according to eq 1, taking into account the preresonance

$$\beta = (3h^2/2m) \frac{W}{(W^2 - h^2\omega^2)(W^2 - 4h^2\omega^2)} \quad (1)$$

factor<sup>1,2</sup> based on the  $\lambda_{\text{max}}$ , where  $W$  is the frequency of the first excited electronic state, and  $\omega$  the fundamental frequency. The results together with corresponding literature values for the planar nonchiral reference compounds 2a-e are presented in Table I.<sup>11,12</sup>

Table I shows that the dipole moments<sup>12</sup> of compounds 1a-c are different from their *N,N*-dimethylaniline analogues 2a-c. This difference might be due to the two nonconjugated cyano groups in the molecules. The vectorial contribution of the cyano dipole moments to the overall dipole moment will be relatively large, with the result that the overall dipole moment axis will not completely coincide with the D- $\pi$ -A axis of the molecule. For compounds 1d,e the dipole moments are found to be more comparable with the reference compounds. In these derivatives, the strong D- $\pi$ -A dipole dominates strongly the value of the overall dipole moment and will therefore almost coincide with this axis.

The absorption maxima of all pyrrolo[1,2-a]quinoline derivatives are in the same wavelength region as the reference materials and are thus largely determined by the acceptor group.

The  $\beta_z$  (1910 nm) values of the substituted pyrrolo[1,2-a]quinolines and the *N,N*-dimethylanilines 2a-e show the same tendency upon variation of the substituents.

**Kurtz Powder Test.** The Kurtz powder method<sup>9</sup> at 1064 nm was used to determine second harmonic genera-

(10) van Hulst, N. F.; Heesink, G. J. T.; Bölger, B.; Kelderman, E.; Verboom, W.; Reinhoudt, D. N. *Proc. SPIE* 1990, 1361, 581.

(11) Cheng, L.-T.; Tam, W.; Meredith, G. R.; Rikken, G. L. J. A.; Meijer, E. W. *Proc. SPIE* 1989, 1147, 61.

(12) McClellan, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman and Company: San Francisco, 1963.

Table II. Powder Survey Results for Particle Sizes within the Range 75–106  $\mu\text{m}$ 

compd	space group	phase matchable	$I_{\text{mat}}(2\omega)/I_{\text{urea}}(2\omega)$	$\lambda_{\text{cutoff}}^c$ nm	color	eff transm rel to urea
$\alpha$ -SiO <sub>2</sub>	P321	no	$0.011 \pm 0.002$	180	white	$0.7 \pm 0.3$
Urea	P42 <sub>1</sub> m	yes	1	200	white	1
MNA	Cc	yes	$5.6 \pm 0.5$	600	yellow	$0.040 \pm 0.015$
1a		no	$0.17 \pm 0.01$	<350	white	$0.6 \pm 0.2$
1b	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	yes	$3.2 \pm 0.2$	<350	white	$0.6 \pm 0.2$
1c	P2 <sub>1</sub>	yes	$1.7 \pm 0.1$	510	yellow	$0.3 \pm 0.1$
1d <sup>a</sup>		yes	$10 \pm 2$	540	yel/orange	$0.010 \pm 0.005$
1d <sup>b</sup>		yes	$0.027 \pm 0.006$	540	yel/orange	$0.010 \pm 0.005$
1e		yes	$0.067 \pm 0.015$	620	orange	$(7 \pm 2) \times 10^{-4}$

<sup>a</sup>Crystallized from methanol. <sup>b</sup>Crystallized from dichloromethane/petroleum ether. <sup>c</sup> $\lambda_{\text{cutoff}}$  is the wavelength at which the powder transmittance is 50%.

tion (SHG) and the phase-matching (PM) ability of the materials in their crystalline form. Urea,  $\alpha$ -quartz, and 2-methyl-4-nitroaniline (MNA, crystals grown from a methanol solution) were used as reference materials in the Kurtz test. The second harmonic intensity  $I(2\omega)$ , measured for the materials as a function of the particle size (relative to urea with a particle size of 75–106  $\mu\text{m}$ ), is shown in Figure 1.

For most materials an increased second harmonic signal with increasing particle size was observed, which indicates phase matching. A second indication of phase-matching ability was a sharp increase of the intensity of the second harmonic radiation upon specific orientations of the samples. Only for quartz and 1a was a decrease of intensity for larger particle sizes observed, which points to a destructive interference of the second harmonic radiation due to non-phase-matching ability. For the dicyanovinyl derivative 1d two sets of values could be obtained, one for crystals obtained from a methanol solution, and the other for crystals obtained from a dichloromethane/petroleum ether solution. To estimate the effects of intrinsic absorption and scattering on the intensity of the generated second harmonic signal, we determined the cutoff wavelength and the effective transmission at 532 nm of the powders (relative to urea). For 1a and 1b no absorption of the second harmonic signal occurred within the transparency range of the microscopic slides of the sample cell. The powder survey results for the particle size range 75–106  $\mu\text{m}$  is given in Table II.

The second harmonic intensities of the reference materials are determined by the phase-matching coefficients  $d_{11} = 0.5$  pm/V for quartz,<sup>2</sup>  $d_{14} = 1.4$  pm/V for urea,<sup>2</sup> and  $d_{12} = 38$  pm/V for 2-methyl-4-nitroaniline (MNA).<sup>13</sup> For MNA the large non-phase-matchable coefficient  $d_{11} = 250$  pm/V also contributes slightly to the observed signal.<sup>13</sup> The determined second harmonic ratio for MNA relative to quartz ( $510 \pm 100$ ) agrees well with that of 375 reported by Williams.<sup>1</sup> The observed signal ratio between urea and quartz ( $91 \pm 15$ ) is below the ratio of 400 reported by Kurtz<sup>9</sup> but agrees reasonably with the value found by Nicoud ( $45 \pm 25$ ).<sup>2</sup> However, it should be noted that the value of Kurtz seems to overestimate the efficiency of urea.<sup>2</sup> Starting from  $d_{\text{quartz}} = 0.50 \pm 0.08$  pm/V and taking into account the effective transmission and assuming a linear model, we calculated from our results  $d_{\text{urea}} = 2 \pm 1$  pm/V and  $d_{\text{MNA}} = 30 \pm 12$  pm/V, which is in agreement with the literature (vide supra). The nonlinear coefficient of 1a is a few times larger than that of quartz, as was previously found for the 5-methyl-substituted analogue of 1a.<sup>10</sup> Again taking into account the effective transmission of the materials, the phase-matching nonlinear coefficients of 1b–d (PE) are 1 order of magnitude lower than that of

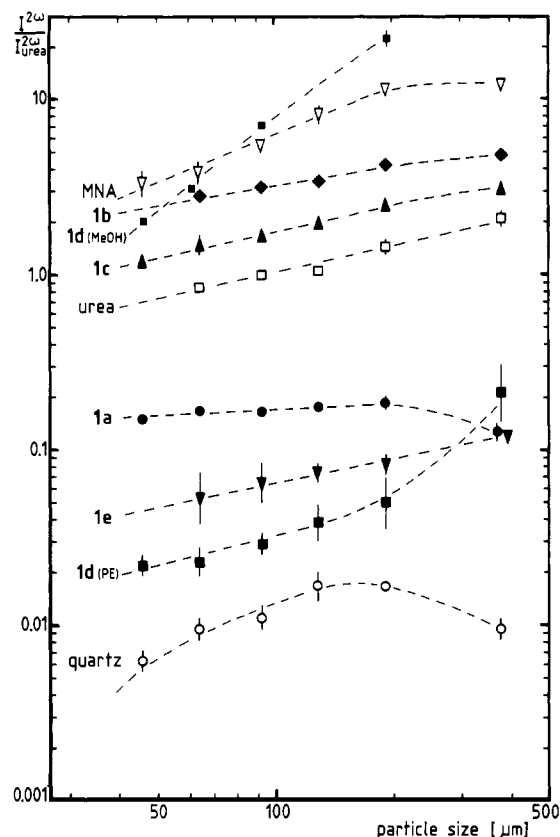


Figure 1. Measured second harmonic intensity  $I(2\omega)$  at 532 nm, as a function of particle size, relative to urea at 75–106  $\mu\text{m}$  for the pyrrolo[1,2-*a*]quinolines 1a–e (filled symbols) and reference materials (open symbols).

MNA. For 1e the phase-matching nonlinear coefficient is of the same order of magnitude as that of MNA. In the powders of 1d and 1e some needlelike crystals were observed, whereas the ideal Kurtz powder test assumes spherical particles. Their influence of the Kurtz signal could not be taken into account. Of special interest is derivative 1d grown from methanol. The phase-matchable nonlinear coefficient of this material is a few times larger than that of MNA. The large difference in SHG efficiency of crystals of 1d grown from different solutions indicates polymorphism.

**Crystal Structure.** Crystals of the aldehyde 1b and the nitro derivative 1c were studied by single-crystal X-ray diffraction. The extent of out of plane rotation of the nitrogen donor atom, which renders the D- $\pi$ -A system chiral, has been estimated by calculating the average angle between the aromatic ring and the pyrrolidine ring to be  $10 \pm 3^\circ$ .

The out-of-plane rotation of the nitrogen donor atom of the pyrrolo[1,2-*a*]quinolines decreases the extent of

(13) Levine, B. F.; Bethea, C. G.; Thurmond, C. D.; Lynch, R. T.; Bernstein, J. L. *J. Appl. Phys.* 1979, 50, 2523.

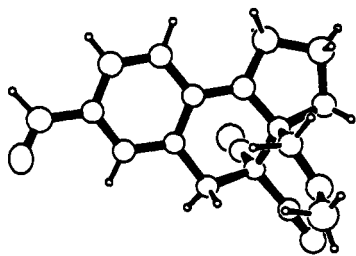


Figure 2. ORTEP drawing of the aldehyde 1b (space group  $P2_12_12_1$ ).

$\pi$ -conjugation and will therefore lower the  $\beta$  value compared to a completely conjugated planar system. Leung et al.<sup>14</sup> have shown that the decrease of the  $\beta$  value is proportional to the cosine of the angle between donor (or acceptor) and conjugated system. For an out-of-plane rotation of  $10^\circ$ , the value of  $\beta$  decreases with 2%, which is negligible within the experimental error.

The aldehyde 1b crystallizes in the space group  $P2_12_12_1$  with a contribution of 8.3% of  $\beta$  under optimal phasematch conditions, while the maximum possible contribution for this space group is 19.2%.<sup>2</sup> The phase-matching ability and the low absorption maximum renders 1b an interesting candidate for further NLO material research (Figure 2).

The nitro derivative 1c crystallizes within the ideal<sup>2</sup> space group  $P2_1$  with two independent molecules within the unit cell. The maximum contribution of  $\beta$  under optimal phase-matching conditions in this space group is 38% if the angle of the D- $\pi$ -A axis with the optical axis is  $54.7^\circ$  and the material is phase matchable in the optimal direction. For the two molecules in the unit cells, angles of  $71.7^\circ$  (28.3% absolute, 74% relative efficiency) and  $43.5^\circ$  (34.3% absolute, 90% relative efficiency) are found. For NPP, which crystallizes in the same  $P2_1$  space group and has a 99% relative efficiency, a powder efficiency of about 150 times urea was observed due to the fact that this material is phase matchable in nearly the optimal direction. The observed powder SHG efficiency of about 1.7 times urea for 1c indicates that the crystal is not phase matchable in the optimal direction (Figure 3).

### Conclusions

In conclusion, the chiral, acceptor-substituted pyrrolo-[1,2-*a*]quinolines are a novel class of second-order nonlinear optical materials, which have comparable hyperpolarizabilities as their *N,N*-dimethylaniline analogues. For all acceptor-substituted derivatives, phase-matching ability of the generated second harmonic is observed.

### Experimental Section

**Synthesis.** Pyrrolidine (Merck), phosphorus oxychloride (Fluka), and malononitrile (Merck) were used without further purification. *p*-Nitrobenzyl phosphonate was synthesized according to the literature.<sup>15</sup> All solvents were freshly distilled prior to use, and all reactions were carried out under an argon atmosphere. The petroleum ether (PE) used had a boiling point range of 40–60  $^\circ\text{C}$ . The synthesis of compound 1a has been described in ref 6.

Melting points were determined with a Reichert melting point apparatus and are uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a Nicolet NT-200 or a Bruker AC 250 spectrometer in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as internal standard. Mass spectra

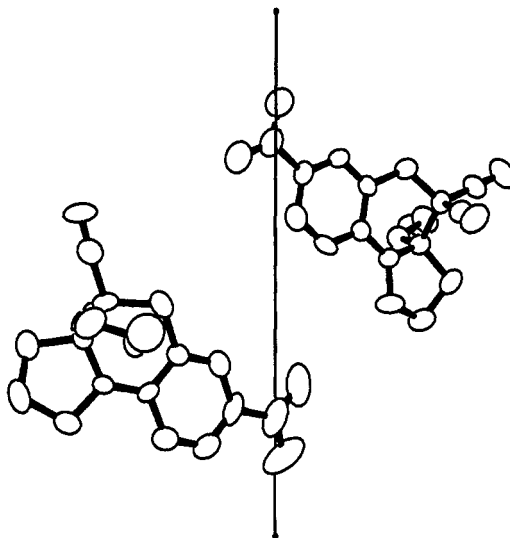


Figure 3. ORTEP drawing of the two independent molecules in the unit cell of the nitro derivative 1c (space group  $P2_1$ ). The angle of the D- $\pi$ -A axis with the plotted optical *b* axis is  $43.5^\circ$  and  $71.7^\circ$  for the two molecules.

were obtained using a Finnigan MAT 90 spectrometer and IR spectra using a Nicolet 5SXC FT-IR spectrophotometer. Optical rotations were determined with a Perkin-Elmer 241 polarimeter, and UV-vis spectra were recorded on a Philips PU 8700 series UV-visible spectrophotometer.

**7-Formyl-1,2,3,3a-tetrahydro-3a-(methoxymethyl)pyrrolo[1,2-*a*]quinoline-4,4(5*H*)-dicarbonitrile (1b).** To a solution of 1a<sup>6</sup> (1.75 g, 6.22 mmol) in *N,N*-dimethylformamide (50 mL) was added phosphorus oxychloride (0.57 mL, 6.22 mmol) in 5 min at 0  $^\circ\text{C}$ . The mixture was refluxed for 18 h, after which no further conversion of 1a to 1b was observed. The mixture was allowed to cool, water (100 mL) and ethyl acetate (100 mL) were added, and the layers were separated. The ethyl acetate layer was subsequently washed with a saturated ammonium chloride solution ( $3 \times 100$  mL) and water ( $3 \times 100$  mL). The organic layer was dried ( $\text{MgSO}_4$ ), and the solvent removed under reduced pressure. The residue was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ) to give 0.77 g (2.74 mmol, 44%) of unreacted 1a and 0.35 g (1.12 mmol, 18%) of 1b: mp 139–140  $^\circ\text{C}$  (MeOH);  $[\alpha]_D^{25} = +121^\circ$  (*c* 0.59,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR  $\delta$  9.78 (s, 1 H, CHO), 7.75–7.65 (m, 2 H, Ar H-8 and Ar H-6), 6.73 (d, 1 H,  $J = 8.5$  Hz, Ar H-9), 3.9–3.4 (m, 6 H,  $\text{ArCH}_2$ ,  $\text{CH}_2\text{OCH}_3$ ,  $\text{NCH}_2$ ), 3.29 (s, 3 H,  $\text{CH}_2\text{OCH}_3$ ), 2.6–2.1 (m, 4 H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR  $\delta$  190.1 (d, CHO), 146.4 (s, C-9a), 131.7 and 130.9 (d, Ar C), 126.5 (s, C-7), 114.0, 113.9 and 113.8 (s, C-5a and CN), 112.9 (d, Ar C-9), 73.3 (t,  $\text{CH}_2\text{OCH}_3$ ), 66.2 (s, C-3a), 59.5 (q,  $\text{CH}_2\text{OCH}_3$ ), 49.7 (t,  $\text{NCH}_2$ ), 36.8 (s,  $\text{C}(\text{CN})_2$ ), 34.3, 33.2 and 21.8 (t,  $\text{ArCH}_2$  and  $\text{CH}_2$  ring); IR (KBr) 2254 (CN), 2763 (CHO)  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  295.132 ( $\text{M}^+$ , calcd 295.132); UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}} = 331$  nm,  $\epsilon = 29500$  L  $\text{mol}^{-1}$   $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2$  ( $M_r$  295.340): C, 69.14; H, 5.80; N, 14.23. Found: C, 69.64; H, 5.80; N, 14.73.

**7-Nitro-1,2,3,3a-tetrahydro-3a-(methoxymethyl)pyrrolo[1,2-*a*]quinoline-4,4(5*H*)-dicarbonitrile (1c).** To a stirred solution of 1a<sup>6</sup> (0.25 g, 0.80 mmol) in dichloromethane (15 mL) was added 65% nitric acid (0.2 mL, 2.9 mmol) in one portion at room temperature. After 30 min a saturated solution of sodium hydrogen carbonate (30 mL) was added and the layers were separated. The water layer was extracted with dichloromethane ( $3 \times 25$  mL). The collected organic layers were washed with water ( $3 \times 25$  mL) and dried over magnesium sulfate. The solvent was evaporated under reduced pressure. The product was obtained by recrystallization of the residue from methanol to yield 0.19 g (0.60 mmol, 75%) of 1c: mp 185–186  $^\circ\text{C}$  (MeOH);  $[\alpha]_D^{25} = +226^\circ$  (*c* 0.42,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR  $\delta$  8.1–8.0 (m, 2 H, Ar H-6 and Ar H-8), 6.66 (d, 1 H,  $J = 9.1$  Hz, Ar H-9), 3.9–3.3 (m, 6 H,  $\text{ArCH}_2$ ,  $\text{CH}_2\text{OCH}_3$ ,  $\text{NCH}_2$ ), 3.30 (s, 3 H,  $\text{CH}_2\text{OCH}_3$ ), 2.6–2.15 (m, 4 H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR  $\delta$  146.6 (s, C-9a), 138.2 (s, C-7), 125.4 and 125.3 (d, Ar C), 113.7, 113.6 and 113.4 (s, C-5a and CN), 112.2 (Ar C-9), 73.5 (t,  $\text{CH}_2\text{OCH}_3$ ), 66.4 (s, C-3a), 59.5 (q,  $\text{CH}_2\text{OCH}_3$ ), 49.0 (t,  $\text{NCH}_2$ ), 36.9 (s,  $\text{C}(\text{CN})_2$ ), 34.4, 33.3 and 21.7 (t,  $\text{ArCH}_2$  and  $\text{CH}_2$  ring); IR

(14) Leung, P. C.; Stevens, J.; Harestad, R. E.; Spiering, M. S.; Gerbi, D. J.; Francis, C. V.; Trend, J. E.; Tiers, G. V. D.; Boyd, G. T.; Ender, D. A.; Williams, R. C. *SPIE* 1989, 1147, 48.

(15) Arbuzov, B. A. *Pure Appl. Chem.* 1964, 9, 307.

(KBr) 2250 (CN)  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  312.122 ( $\text{M}^+$ , calcd 312.122); UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}} = 372 \text{ nm}$ ,  $\epsilon = 18\,200 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_3$  ( $M_r$  312.327): C, 61.53; H, 5.16; N, 17.94. Found: C, 61.42; H, 5.45; N, 17.83.

**7-(1,1-Dicyanoethenyl)-1,2,3,3a-tetrahydro-3a-(methoxymethyl)pyrrolo[1,2-a]quinoline-4,4(5H)-dicarbonitrile (1d).** To a solution of **1b** (0.10 g, 0.32 mmol) in toluene (10 mL) was added malononitrile (0.02 g, 0.32 mmol) in one portion. After stirring for 2 h at room temperature the solvent was removed under reduced pressure to yield 0.10 g (0.28 mmol, 87%) of **1d** after recrystallization of the residue from ethanol: mp 182–184 °C (EtOH);  $[\alpha]_D^{25} = +241^\circ$  ( $c$  0.52,  $\text{CHCl}_3$ );  $^1\text{H NMR}$   $\delta$  7.80 (d, 1 H,  $J = 8.8 \text{ Hz}$ , Ar H-8), 7.72 (s, 1 H, Ar H-6), 7.53 (s, 1 H, CH=), 6.72 (d, 1 H,  $J = 8.8 \text{ Hz}$ , Ar H-9), 3.9–3.3 (m, 6 H,  $\text{ArCH}_2$ ,  $\text{CH}_2\text{OCH}_3$  and  $\text{NCH}_2$ ), 3.31 (s, 3 H,  $\text{CH}_2\text{OCH}_3$ ), 2.5–2.2 (m, 4 H,  $\text{CH}_2$ );  $^{13}\text{C NMR}$   $\delta$  158.0 (d, CH=), 146.9 (s, C-9a), 133.3 and 132.6 (d, Ar C), 113.5 (d, Ar C-9), 120.8 and 115.0 (s, C-7 and C-5a), 73.7 (t,  $\text{CH}_2\text{OCH}_3$ ), 66.7 (s, C-3a), 59.7 (q,  $\text{CH}_2\text{OCH}_3$ ), 49.0 (t,  $\text{NCH}_2$ ), 37.1 (s,  $\text{C}(\text{CN})_2$ ), 34.5, 33.4 and 21.9 (t,  $\text{ArCH}_2$  and  $\text{CH}_2$  ring); IR (KBr) 2218 (CN)  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  343.143 ( $\text{M}^+$ , calcd 343.143); UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}} = 418 \text{ nm}$ ,  $\epsilon = 50\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{17}\text{N}_5\text{O}_3$  ( $M_r$  343.387): C, 69.96; H, 4.99; N, 20.39. Found: C, 69.65; H, 5.03; N, 20.44.

**7-[1-(4-Nitrophenyl)ethenyl]-1,2,3,3a-tetrahydro-3a-(methoxymethyl)pyrrolo[1,2-a]quinoline-4,4(5H)-dicarbonitrile (1e).** *p*-Nitrobenzyl phosphonate (0.18 g, 0.66 mmol) dissolved in toluene (20 mL) was added in one portion to a washed sodium hydride (0.03 g, 1 mmol) suspension in toluene (30 mL) and stirred for 1 h. A solution of aldehyde **1b** (0.20 g, 0.65 mmol) in toluene (10 mL) was added dropwise in 5 min, and subsequently the reaction mixture was refluxed for 24 h. The mixture was allowed to cool, and water (25 mL) was added. The organic layer was separated and the water layer was extracted with dichloromethane ( $3 \times 10 \text{ mL}$ ). The combined organic layers were dried ( $\text{MgSO}_4$ ), and the solvents removed under reduced pressure. The residue was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ) to yield 0.21 g (0.48 mmol, 75%) of **1e**: mp 246–248 °C (MeOH);  $[\alpha]_D^{25} = +214^\circ$  ( $c$  0.38,  $\text{CHCl}_3$ );  $^1\text{H NMR}$   $\delta$  8.20 (d, 2 H,  $J = 8.7 \text{ Hz}$ , Ar H), 7.58 (d, 2 H,  $J = 8.7 \text{ Hz}$ , Ar H), 7.42 (d, 1 H,  $J = 8.5 \text{ Hz}$ , Ar H-8), 7.30 (s, 1 H, Ar H-6), 7.24 (d, 1 H,  $J = 16.3 \text{ Hz}$ , CH=CH), 6.96 (d, 1 H,  $J = 16.3 \text{ Hz}$ , CH=CH), 6.69 (d, 1 H,  $J = 8.5 \text{ Hz}$ , Ar H-9), 3.6–3.2 (m, 6 H,  $\text{ArCH}_2$ ,  $\text{CH}_2\text{OCH}_3$ ,  $\text{NCH}_2$ ), 3.32 (s, 3 H,  $\text{CH}_2\text{OCH}_3$ ), 2.7–2.1 (m, 4 H,  $\text{CH}_2$ );  $^{13}\text{C NMR}$   $\delta$  146.0 (s, C-9a), 126.1 and 124.0 (d,  $\text{ArNO}_2$  C), 73.3 (t,  $\text{CH}_2\text{OCH}_3$ ), 66.2 (s, C-3a), 59.5 (q,  $\text{CH}_2\text{OCH}_3$ ), 48.8 (t,  $\text{NCH}_2$ ), 36.8 (s,  $\text{C}(\text{CN})_2$ ), 34.5, 33.3 and 22.0 (t,  $\text{ArCH}_2$  and  $\text{CH}_2$  ring); IR (KBr) 2251 (CN)  $\text{cm}^{-1}$ ; mass spectrum,  $m/e$  414.169 ( $\text{M}^+$ , calcd 414.169); UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}} = 417 \text{ nm}$ ,  $\epsilon = 30\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_3$  ( $M_r$  414.463): C, 69.55; H, 5.35; N, 13.52. Found: C, 69.57; H, 5.57; N, 13.09.

**EFISH Measurements.** As a source of fundamental radiation a 1.064- $\mu\text{m}$  10-Hz pulsed Nd:YAG laser with seeder was used. The laser beam is passed through a RG830 visible filter and is focused into the EFISH cell. The harmonic light is filtered out with an IR cutoff filter and a 532-nm interference filter. The second harmonic light is detected with a photomultiplier and analyzed with a boxcar integrator and a computer. The EFISH cell consists of two BK7 windows which form a wedge with an angle of about  $1^\circ$ . The distance between the windows is 0.1–0.2 mm, and the distance between the high voltage electrodes is 3 mm. This cell is mounted on a translation stage, so that it can be displaced perpendicularly to the laser beam. This enables changing the path length continuously. If the second harmonic intensity is measured as a function of the path length, one obtains a sinusoidal interference pattern. A quartz wedge which is used as a reference, is mounted on the same translation stage.

The analysis points were fitted to a sine-squared function.<sup>16</sup> This fit provides the SHG amplitude and the coherence length. The third-order susceptibility  $\Gamma$  value of the solution is calculated with the help of the data recorded for the quartz wedge.<sup>17,18</sup> For

each compound five different solutions in the 0.1–1.0 mM concentration range were measured. From the value of  $\Gamma$  as a function of concentration,  $\gamma^{\text{EFISH}}$  can be deduced from eq 2.

$$\gamma^{\text{EFISH}} = \gamma_e + \mu\beta/5kT \quad (2)$$

The  $\gamma_e$  term is the electronic part of the second-order hyperpolarizability and is usually negligibly small<sup>1,17,18</sup> compared to the second term and is therefore neglected in our calculations. With the knowledge of the dipole moment  $\mu$ , the hyperpolarizability  $\beta_z$  of the molecules can be calculated. In the calculations of the  $\beta_z$  values, both vectors  $\mu\beta$  and  $\mu$  are assumed to be parallel.

**Dipole Moment Measurements.** The dipole moment of the pyrrolo[1,2-a]quinoline derivatives was obtained by measuring the dielectric constant of five different solutions in the 0.1–1.0 mM concentration range. The data were analyzed according to the equation of Onsager.<sup>17</sup>

**Kurtz Powder Test.** Crystalline powders were obtained by grinding larger single crystals using a ball mill. The powders were graded to the desired range of particle sizes using a standard set of sieves. The sample cell consisted of two microscopic slides separated by a spacer of 500  $\mu\text{m}$  thickness.

As a source of fundamental radiation a 1.064- $\mu\text{m}$  pulsed Nd:YAG laser (Spectra Physics DCR 11 3G, 10 Hz,  $T_{\text{pulse}} \approx 10 \text{ ns}$ ) was used. The laser beam was directed onto the sample cell with 3-mm beam diameter and  $\sim 10\text{-mJ}$  pulse energy. The generated second harmonic in the forward direction was collimated with a 0.54 NA lens. Separation of fundamental and second harmonic radiation was achieved by use of a suitable filter set and a monochromator. As a detector for the second harmonic radiation, a photomultiplier tube and boxcar averager were used. Care was taken to keep the signal levels within the linear range of the photomultiplier. To this purpose a calibrated set of filters was used.

**X-ray Diffraction.** Crystal data **1b**:  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2$ , orthorhombic, space group  $P2_12_12_1$ ;  $a = 9.738$  (5) Å,  $b = 10.078$  (6) Å,  $c = 15.387$  (8) Å,  $V = 1510 \text{ Å}^3$ ;  $Z = 4$ ;  $d_{\text{calc}} = 1.30 \text{ g cm}^{-3}$ ,  $\mu = 0.82 \text{ cm}^{-1}$ . Reflections were measured in the  $\omega/2\theta$  scan mode, using graphite-monochromated Mo K $\alpha$  radiation [scan width ( $\omega$ )  $1.10 + 0.34 \tan \theta$ ,  $3 < \omega < 30^\circ$ ]. The structure was solved by direct methods and refined with full-matrix least-squares methods. A total of 1554 reflections with  $F_o^2 > 2\sigma(F_o^2)$  was used in the refinement. The number of parameters refined was 268 [scale factor, extinction parameter, positional parameters of all atoms, and thermal parameters (isotropic for H atoms, anisotropic for others)]. The final  $R$  factors were  $R = 3.1\%$ ,  $R_w = 3.2\%$ . All calculations were done with SDP.<sup>19</sup>

Crystal data **1c**:  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_3$ , monoclinic, space group  $P2_1$ ;  $a = 8.796$  (6) Å,  $b = 12.761$  (8) Å,  $c = 14.010$  (8) Å,  $V = 1555 \text{ Å}^3$ ;  $Z = 4$ ;  $d_{\text{calc}} = 1.34 \text{ g cm}^{-3}$ ,  $\mu = 0.90 \text{ cm}^{-1}$ . Reflections were measured in the  $\omega/2\theta$  scan mode, using graphite-monochromated Mo K $\alpha$  radiation [scan width ( $\omega$ )  $1.40 + 0.6 \tan \theta$ ,  $3 < \omega < 27.5^\circ$ ]. The structure was solved by direct methods and refined with full-matrix least-squares methods. A total of 1959 reflections with  $F_o^2 > \sigma(F_o^2)$  was used in the refinement. The number of parameters refined was 415 [scale factor, extinction parameter, positional and anisotropic thermal parameters of the non-H atoms; H atoms were treated as riding atoms]. The final  $R$  factors were  $R = 7.0\%$ ,  $R_w = 6.3\%$ . The crystal structure of **1c** contains two independent molecules, which differ slightly in the orientation of the  $\text{CH}_2\text{OCH}_3$  groups.

In both structures the absolute configuration was not determined but has been assumed to be the one of the starting material **1a**.<sup>6</sup>

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(16) Teng, C. C.; Garito, A. F. *Phys. Rev. B* 1983, 28, 6766.

(17) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* 1975, 63, 2666.

(18) Huijts, R. A.; Hesselink, G. L. *J. Chem. Phys. Lett.* 1989, 156, 209.

(19) *Structure Determination Package*; B. A. Frenz and Associates Inc.: College Station, TX; and Enraf-Nonius: Delft, The Netherlands, 1983.

the Foundation for Fundamental Material Research (FOM) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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**Supplementary Material Available:** Structures of 1b and 1c and tables of positional and thermal parameters, bond distances and angles (10 pages). Ordering information is given on any current masthead page.

## Hydrogen-Induced Disproportionation of the Intermetallic Compound ZrCo

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Disproportionation of the intermetallic compound ZrCo in the presence of hydrogen into ZrH<sub>2</sub> and ZrCo<sub>2</sub> has been observed in the temperature range 350–500 °C during both the absorption and the desorption mode. Quantitative reproporationation into ZrCo can be achieved by vacuum annealing at high temperatures. The resistance of a sample toward degradation was found to be determined by its previous history.

### Introduction

ZrCo<sup>1-3</sup> can be considered as one of the most promising getters to replace uranium (present reference material) for the handling, transport, and storage of tritium in the fuel cycle of future fusion devices.<sup>4</sup> At a typical storage temperature of 25 °C, ZrCo hydride has an equilibrium pressure of about 10<sup>-3</sup> Pa in the absorption mode, provided the amount of stored gas is limited to a plateau region of 0 < n<sub>Q</sub>/n<sub>ZrCo</sub> < 2.7 (Q = H, D, or T). The immobilized gas can be recovered at moderate temperatures, e.g., as deduced from isopleth experiments, a H<sub>2</sub> equilibrium pressure of 1 bar is attained at only 375 °C.<sup>2</sup> In addition, from the point of view of safety, ZrCo and its hydride have proven to be much less pyrophoric than uranium and its hydride. To complete the data base needed for the evaluation of ZrCo as a getter material for use in tritium technology, work is presently in progress in our laboratories on (i) the solubility of hydrogen isotopes in ZrCo,<sup>5</sup> (ii) the aging of ZrCo tritide,<sup>6</sup> and (iii) the definition of the stability range of the ternary hydride ZrCoH<sub>x</sub>.

Previously, we reported that ZrCo samples can be submitted to 35 loading/deloading cycles at room temperature employing 100 kPa of H<sub>2</sub> to load and 1.5 h at 450 °C under a vacuum of 10<sup>-4</sup> Pa to deload without loss in storage

capacity or change in the hydriding kinetics.<sup>1</sup> Using relatively large amounts of ZrCo (25 g) Shmayda et al.<sup>7</sup> recently observed a deterioration in loading kinetics after the sample had undergone a steep temperature rise to 400 °C in the deloading mode. To clarify this discrepancy, we investigated systematically the effect of high temperatures (>400 °C) and high pressures (>100 kPa) on the stability of the intermetallic hydride ZrCoH<sub>x</sub>.

### Experimental Section

**Reagents.** Ingots of the intermetallic compound ZrCo were purchased from SAES Getters, Milano, Italy. The activation procedure, resulting in the formation of a homogeneous powder, and the characterization by X-ray diffraction, microprobe analysis, and conventional surface analytical techniques of the starting and the activated materials were as reported in a previous publication.<sup>2</sup> Prior to an experiment, the activated ZrCo powder was always subjected to two additional loading/deloading cycles, i.e., (i) loading with 10 kPa of H<sub>2</sub> at room temperature up to the stoichiometrical composition ZrCoH<sub>3</sub> and (ii) deloading while heating for 1.5 h at 450 °C under a vacuum of 10<sup>-4</sup> Pa.

The purity and purification method of gaseous hydrogen and deuterium are as described in ref 2.

**Apparatus.** Loading/deloading experiments at pressures up to 1.2 × 10<sup>5</sup> Pa were carried out in an apparatus described in detail elsewhere.<sup>2</sup>

For the investigations at pressures up to 4 MPa, a Nimonic autoclave with a volume of 0.01 L manufactured by NOVA Swiss, Effretikon, Switzerland, was used. The autoclave is equipped with two pressure sensors type 8210 from Burster Präzisionsmesstechnik, Gernsbach, Germany, operating in the pressure ranges (1–5) × 10<sup>5</sup> or (1–50) × 10<sup>5</sup> Pa, respectively. The autoclaves were externally heated in an oven of large heat capacity, whose temperature could be held constant to ±1 °C with Eurotherm, Limburg, Germany, controllers. To avoid direct contact of the ZrCo powder with the metallic surface of the autoclave the samples (approximately 1 g) were placed inside of a quartz tube. Three axially positioned Ni/NiCr thermocouples located at different heights within the quartz tube served to register the

(1) Penzhorn, R.-D.; Devillers, M.; Sirch, M. *J. Nucl. Mater.* 1990, 170, 217.

(2) Devillers, M.; Sirch, M.; Bredendiek-Kämper, S.; Penzhorn, R.-D. *Chem. Mater.* 1990, 2, 255.

(3) Konishi, S.; Nagasaki, T.; Yokokawa, N.; Naruse, Y. *Fusion Eng. Design* 1989, 10, 355.

(4) Leger, D.; Dinner, P.; Yoshida, H.; Fleming, R.; Anderson, J.; Andreev, A.; Asahara, M.; Boissin, J. C.; Finn, P.; Gouge, M.; Iseli, M.; Kapishev, V.; Kabaashi, S.; Kuteev, B.; Kveton, O.; Muller, M.; Murdoch, D.; Nagashima, K.; Nasise, J.; Penzhorn, R.-D.; Sebnennikov, D. V.; Shantalov, G.; Sherman, R.; Suzukii, T.; Sze, D.; Tanemori, N.; Vasil'ev, V.; Willms, S. *ITER Fuel Cycle*; ITER Documentation series No 31, IAEA, Vienna, 1991.

(5) Devillers, M.; Sirch, M.; Penzhorn, R.-D., to be published.

(6) Ache, H. J.; Glugla, M.; Hutter, E.; Jourdan, G.; Penzhorn, R.-D.; Röhrig, D.; Schubert, K.; Sebnening, H.; Vetter, J. E. *Fusion Eng. Design* 1990, 12, 331.

(7) Shmayda, W. T.; Heics, A. G.; Kherani, N. P. *J. Less Comm. Met.* 1990, 162, 117.