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Reactions of 2*H*-3,4-Dihydro-1,4-benzoxazin-6(8a*H*)-ones with 2,4,6-Trimethylbenzonitrile Oxide, III [1]#

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Summary. Regio-, stereo- and siteselectivity of the cycloadditions of trimethylbenzonitrile oxide with 2*H*-3,4-Dihydro-1,4-benzoxazin-6(8a*H*)-ones have been investigated. The structures of the obtained products were elucidated by means of homonuclear NOE difference spectroscopy and HMQC and HMBC spectra. The structure of 6-Benzyl-9a-methoxy-3-mesityl-9b-methyl-7,8,9a,9b-tetrahydro-3a*H*-1,2-oxazolo-[4,5-h]1,4-benzoxazin-4(6*H*)-on **5** was elucidated from a single crystal X-ray structure analysis at ambient temperature: $C_{27}H_{30}N_2O_4$, M = 446.55 g/mol, monoclinic, $P2_1/c$, $a = 10.372$ (34) Å, $b = 11.908$ (21) Å, $c = 20.040$ (34) Å, $\beta = 97.16$ (17)°, $V = 2455.8$ (1.9) Å^3, $Z = 4$, $d_c = 1.208$ g/cm^3, $\mu = 0.08$ mm^{-1}, $R = 0.0546$.

Keywords. 3,4-Dihydro-1,4-benzoxazin-6(8a*H*)-ones; Nitrile oxide; 1,3-Dipolar cycloaddition; 1,2-Oxazolines; NMR-data; X-ray analysis.

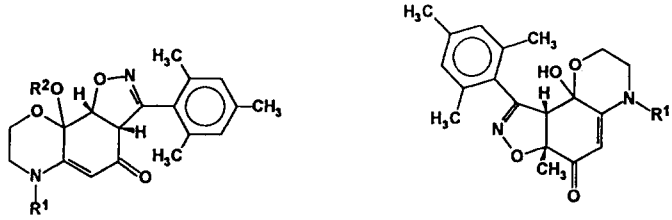
Über die Reaktion von 2*H*-3,4-Dihydro-1,4-benzoxazin-6(8a*H*)-onen mit 2,4,6-Trimethylbenzonitriloxid, III [1]#

Zusammenfassung. Die Regio- und Stereoselektivität der Cycloaddition von Trimethylbenzonitriloxid (*TMBNO*) an 2*H*-3,4-Dihydro-1,4-benzoxazin-6(8a*H*)-one wurde untersucht. Die Strukturen der erhaltenen Produkte wurden durch homonucleare NOE-Differenzspektroskopie und HMQC- und HMBC-Spektren aufgeklärt. Die Struktur von 6-Benzyl-9a-methoxy-3-mesityl-9b-methyl-7,8,9a,9b-tetrahydro-3a*H*-1,2-oxazolo[4,5-h]1,4-benzoxazin-4(6*H*)-on **5** konnte mittels einer Kristallstrukturanalyse bei Raumtemperatur aufgeklärt werden: $C_{27}H_{30}N_2O_4$, M = 446.55 g/mol, monoklin, $P2_1/c$, $a = 10.372$ (34) Å, $b = 11.908$ (21) Å, $c = 20.040$ (34) Å, $\beta = 97.16$ (17)°, $V = 2455.8$ (1.9) Å^3, $Z = 4$, $d_c = 1.208$ g/cm^3, $\mu = 0.08$ mm^{-1}, $R = 0.0546$.

Introduction

2,4,6-Trimethylbenzonitrile oxide (*TMBNO*) reacts with 2-hydroxyethylamino-1,4-benzoquinones and the corresponding quinole derivatives to afford regioselectively tetrahydro-3a*H*-1,2-oxazolo[4,5-h]1,4-benzoxazin-4(6a*H*)-ones **I** [1].

Dedicated to Prof. Ott with best wishes for his 70th birthday



I II

R^1 = alkyl, aralkyl
R^2 = H, CH_3

Fig. 1

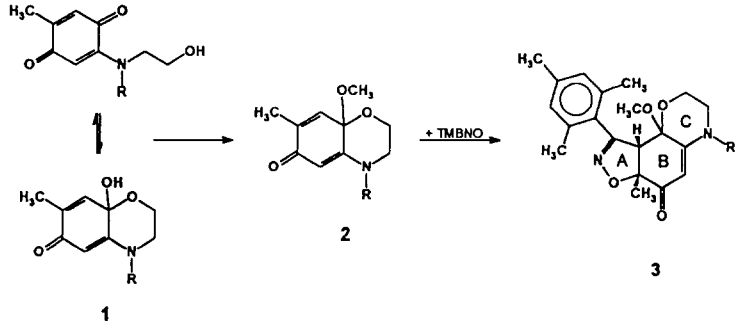
We recently reported about the reactions of hydroxyethylaminotoluquinones. To briefly summarize, a reversal of the direction of addition is occurring presumably due to the substituent at the dipolarophile site. Thus, tetrahydro-2*H*-1,2-oxazolo-[5,4-h]1,4-benzoxazin-6(6a*H*)-ones **II**, which are isomers of entities **I**, are obtained [2].

We here present the results of our studies on cycloaddition reaction of *TMBNO* to 8a-methoxy-7-methyl-2*H*-3,4-dihydro-1,4-benzoxazin-6(8a*H*)-ones **2** with respect to dipolarophilicity, regio- and site selectivity. A series of nuclear *Overhauser* enhancement difference spectra and inverse heteronuclear C, H-correlation spectra allowed us to define the constitution and the conformation of the obtained cyclo-adducts. In order to elucidate the structure of entity **5** a X-ray analysis was carried out.

Results and Discussion

Synthesis

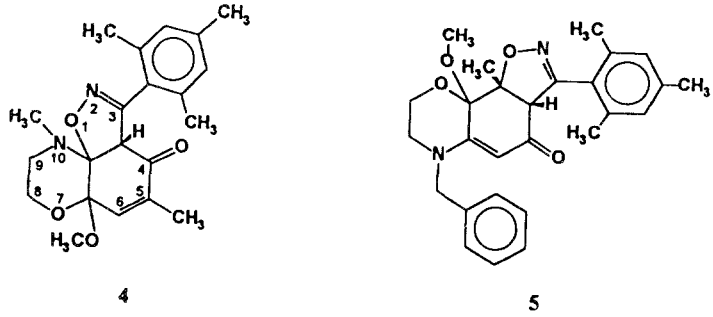
5-Methyl-3,4-dihydrobenzoxazinones **2a** and **2c**, respectively, react with *TMBNO* in boiling methanol more slowly than the analogous benzoquinone derivatives. Thus, the yield of the obtained cycloadducts was rather low.



1 2 3

1 - 3	R
a	CH_3
b	$CH_2C_6H_5$
c	CH_2CH_2OH

Fig. 2



4 5

Fig. 3

Cycloaddition of the dipole *TMBNO* to **2a** affords the complex ring system **3a** along with a compound of an unexpected structure (**4**). In this case the attack of the 1,3-dipole apparently occurred at the vinylogous enamine double bond to afford entity **4**. The reaction of **2b** provides the heterocycle **5** along with the expected cycloadduct **3b**. Rather irritating to us, the angular methyl group of compound **5** is in *meta* position to the nitrogen of the oxazine moiety. The structure of the latter was undoubtedly confirmed by X-ray analysis.

If the reaction we have been looking at is conducted in a non polar aprotic solvent at room temperature, the rate of reaction decreases, the yield thus being very low. However, we were pleased to find that **3c** was produced under these gentle conditions.

NMR-spectroscopy

Nuclear *Overhauser* enhancement (NOE) of the signals in the difference spectra of **3a–c** allowed us to define the way the isoxazoline and the cyclohexene ring are fused. On irradiation of the angular methyl signal, an NOE of the signal due to the adjacent proton H-9b was observed, thereby requiring H-9b to lie on the same side of the ring as the methyl group. This result indicated that the AC ring junction was cis. NOE between H-9b and the *o*-methyl signals of the mesityl moiety again confirmed the outlined constitution of the cycloadducts **3a–c**. ^{13}C resonances were assigned by HMQC [3] (Heteronuclear Multiple-Quantum Coherence experiment: ^{1}H-detected H, C correlation) and HMBC spectra [4] (Heteronuclear Multiple-Bond Connectivity: ^{1}H-detected C, H correlation, optimized for small coupling constants).

X-ray analysis of **5**

Figure 4 shows a stereographic representation of a molecule of **5** in the crystal. The bond lengths and angles and atom labels (number of atoms not corresponding to IUPAC nomenclature) used in the X-ray analysis are summarized in Fig. 5. The mean standard deviation of bond lengths between non-hydrogen atoms is 0.007 Å. No unusual values for bond lengths and angles were observed.

Least squares planes through the atoms of each ring and interplanar angles were calculated in order to describe the overall molecular topology. The plane through atoms C1, N2, O3, C4 and C13 forms an angle of 79.5(2)° with a plane through the

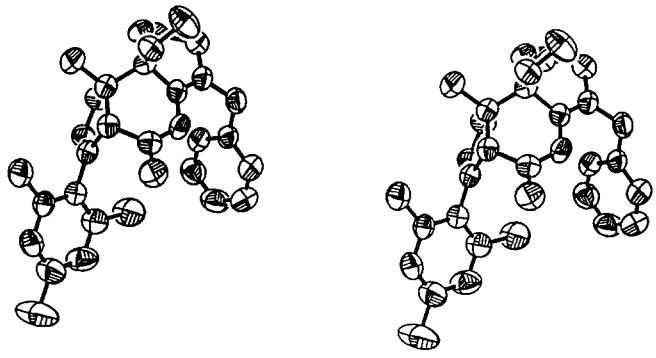


Fig. 4. Ortep drawing of **5**. Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms have been omitted

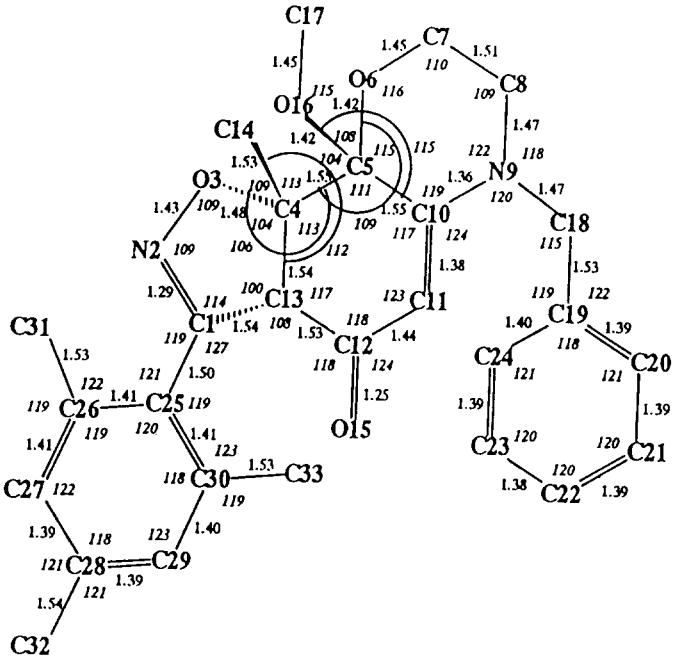


Fig. 5. Atom labels, bond lengths and angles for **5**. Standard deviations for bond lengths are about 0.007 Å, for bond angles 0.4°

atoms of the fused 6-membered ring, the angle between the plane of the phenyl ring with atoms C25 to C30 and the plane through the oxazole moiety is 66.9(2)°. The angle of a plane through atoms C4, C5, C10, C11, C12 and C13 with a plane defined by the atoms of the oxazine (C5, O6, C7, C8, N9, C10) is 25.6(2)°. The oxazine appears in a half-chair conformation, the oxazole is conformed like an envelope.

To briefly summarize, it was found that the LUMO (nitrile oxide)/HOMO (quinone/quinol) interaction is the governing factor in the cycloaddition reaction of *TMBNO* to both hydroxyethylaminobenzo- and toluquinones and to the corresponding quinole derivatives. Thus, we always failed to get C=O adducts.

The loss in reactivity and site-selectivity in the reaction of *TMBNO* to the dipolarophiles **2** may be due to the substitution pattern at the dipolarophilic C=C double bond. Good evidence for steric compression is contained in the reaction of **2a** affording **3a** along with a second C=C adduct (**4**): the bulky benzyle and hydroxyethylamino moiety, respectively, makes the aminesubstituted C=C double bond of quinoles **2b** and **2c** inert to an attack of the 1,3-dipole.

The 1,3-dipolar cycloaddition is a stereospecific *cis*-addition. According to *Huisgen*'s examinations, the experimental results indicate that the majority of the 1,3-dipolar cycloadditions take place concertedly [5]: The new σ-bonds are formed simultaneously, *i.e.* in a one-step process, but not necessarily at the same speed. The substituents on the dipolarophile double bond keep their original position at first. In some 1,3-dipolar cycloadditions, a stabilization of the primary adduct through isomerization with migration of a proton follows the primary step of addition. According to our knowledge, migrations of methyl groups have, however, not yet been observed as a secondary reaction of a 1,3-dipolar cycloaddition. Thus the question arises, whether the reaction of *TMBNO* with **2b** under formation of **5** really is a one-step process, or whether for formation of **5** is not based on a multiple step mechanism, with a migration of the methyl group. In order to find an answer to this question, examinations are being carried out, the results of which will be reported at a later point in time.

Experimental

Melting points were determined on a Tottolli melting point apparatus (*Büchi*) and are uncorrected. The Infrared spectra were taken with a Perkin-Elmer-Gitter-spectrophotometer 225. UV/VIS-spectra were recorded on a Shimadzu-UV-160 A UV/VIS Recording Spectrophotometer. The NMR spectra were obtained on a Bruker AMX-500 spectrometer and on a Bruker AM-200 spectrometer, respectively, using deuteriodimethylsulfoxide as solvent. HMQC: phase-sensitive using TPPI, BIRD sequenz, GARP-decoupled (^{13}C-decoupling: pulse width 60 ms). HMBC: phase-sensitive using TPPI, delay to observe longe-range couplings: 71 ms ($J_{C,H} = 7$ Hz). Mass spectra were recorded with a Varian-Mat-312-Spectrometer with at an ionisation energy of 70 eV. Thin-layer chromatography was performed on precoated plates of silica gel 60 F_{254} (Merck). Column chromatography was carried out on Merck Kieselgel 60 (size 0.063–0.200 mm). In the compounds **3**, **4** and **5**, calculated and actual values for the elementary analyses correspond excellently.

Preparation of starting materials

2*H*-3,4-Dihydro-1,4-benzoxazin-6(8a*H*)-ones **2** were prepared by methylation of the corresponding quinones **1** with methyl iodide, according to a procedure described in the literature [6]. Quinones **1** were synthesized by the method of *König* and *Letsch* [7]. 2,4,6-Trimethylbenzonitrile oxide was prepared according to a well known procedure [8] by oxidation of 2,4,6-trimethylbenzaldoxime.

General Procedure for the reaction of quinoles **2** *with 2,4,6-Trimethylbenzonitrile oxide (TMBNO)*

A solution containing 5 mmoles of the quinole **2** and 8 mmoles of *TMBNO* in 50 ml methanol was heated at reflux for 40–100 h, until the starting nitrile oxide had been consumed, as monitored by TLC (**2c**: chloroform, room temperature, 6 months).

9b-Methoxy-4,6a-dimethyl-9-(2,4,6-trimethylphenyl)-3,4,9a,9b-tetrahydro-2H-1,2-oxazolo[5,4-8]1,4-benzoxazin-6(6aH)-one (**3a**)

The crude entity **3a** was separated on cooling the mixture to room temperature. It was further purified by recrystallization from a mixture of ethanol and ethylacetate.

$C_{21}H_{26}N_2O_4$ (370.5). Yield 7%, m.p. 220 °C. UV/VIS (MeOH): λ_{max} ($\log \varepsilon$) = 249.5 (4.13), 307.5 (4.57). IR (KBr): $\nu = 1626\,cm^{-1}$ (C=O). ^{1}H-NMR (500.13 MHz, *DMSO*-d_6): $\delta = 6.85$, 6.83 (each s, 2H,

m-mesityl), 5.09 (s, 1H, 5-H), 4.45 (s, 1H, 9a-H), 3.67 (m, 1H, 2-H_{pax}[a]), 3.25 (m, 1H, 2-H_{peq}[b]), 3.20 (s, 3H, OCH_3), 2.98 (m, 1H, 3-H_{peq}), 2.76 (s, 3H, NCH_3), 2.5 (m, 1H, 3-H_{pax}), 2.21, 2.19 (each s, 6H, mesityl *o*-methyl), 2.01 (s, 3H, mesityl *p*-methyl), 1.57 (s, 3H, C-6a-CH_3). ^{13}C-NMR (125.75 MHz, *DMSO*-d_6): $\delta = 188.11$ (C-6), 157.08 (C-9 or C-4a), 156.85 (C-4a or C-9), 137.39, 136.74, 135.62 (mesityl C-2, C-4, C-6), 127.99, 127.91 (mesityl C-3 and C-5), 126.66 (mesityl C-1), 100.00 (C-5), 93.02 (C-9b), 85.70 C-6a), 56.92 (C-9a or C-3), 56.82 (C-2 or C-9a), 48.05 (OCH_3), 46.54 (C-3), 38.34 (NCH_3), 20.60, 20.52, 19.55 (mesityl CH_3, C-6a-CH_3). MS (70 eV): *m/z* (%) = 370 [M^+] (32), 298 (28), 169 (88), 154 (100), 82 (40).

6a-Methoxy-5,10-dimethyl-3-(2,4,6-trimethylphenyl)-8,9,10,10a-tetrahydro-3aH-1,2-oxazolo[5,4-e]1,4-benzoxazin-4(6aH)-on (**4**):

After evaporation of the solvent the residue was purified by recrystallization from ethyl acetate to obtain **4**.

$C_{21}H_{26}N_2O_4$ (370.5). Yield 16%, m.p. 224 °C. UV/VIS (MeOH): λ_{max} (log ε) = 236.6 (4.16), 206.8 (4.41). IR (KBr): $\nu = 1691\,cm^{-1}$ (C=O). ^{1}H-NMR (500.13 HMz, *DMSO*-d_6: $\delta = 6.90$ (s, 2H, *m*-mesityl), 6.81 (q, 1H, 6-H), 4.29 (s, 1H, 3a-H), 3.97 (m, 1H, 8-H_{paq}[a]), 3.72 (m, 1H, 8-H_{peq}[b], 3.07 (m, 1H, 9-H_{pax}), 3.05 (s, 3H, OCH_3), 2.54 (m, 1H, 9-H_{peq}), 2.31 (s, 3H, NCH_3), 2.22, 2.10 (each s, 9H, mesityl CH_3), 1.74 (d, 3H, C-5-CH_3). ^{13}C-NMR (125.75 MHz, *DMSO*-d_6: $\delta = 188.43$ (C-4), 151.64 (C-3), 143.95 (C-6), 139.08 (mesityl C-2, C-4, C-6), 128.96 (mesityl C-3, C-5), 123.86 (mesityl C-1), 100.19 (C-10a), 94.27 (C-6a), 62.74 (C-3a), 59.20 (C-8), 47.58 (C-9), 47.47 (OCH_3), 38.11 (NCH_3), 20.84, 20.32 (mesityl CH_3), 14.82 (C-5-CH_3). MS (70 eV): *m/z* (%) = 370 [M^+], 243 (30), 186 (35), 179 (100), 58 (48).

4-Benzyl-9b-methoxy-6a-methyl-9-(2,4,6-trimethylphenyl)-3,4,9a,9b-tetrahydro-2H-1,2-oxazolo[5,4-h]1,4-benzoxazin-6(6aH)-one (**3b**):

After evaporation of the solvent the residue was subjected to column chromatography, using a mixture of benzene and chloroform (1:1) as eluent. **3b** was separated and recrystallized from ethyl acetate. Material eluted from the silica gel with methanol was recrystallized from a mixture of ethanol and ethyl acetate to obtain **5**.

$C_{27}H_{30}N_2O_4$ (446.6). Yield 24%, m.p. 221.5 °C. UV/VIS (MeOH): λ_{max} (log ε) = 249.5 (4.24), 309.5 (4.68). IR (KBr): $\nu = 1610\,cm^{-1}$ (CO). ^{1}H-NMR (500.13 MHz, *DMSO*-d_6): $\delta = 7.27$ (m, 5H, phenyl), 6.89, 6.86 (each s, 2H, *m*-mesityl), 5.15 (s, 1H, 5-H), 4.53, 425 (each d, 2H, CH_2-C_6H_5), 4.50 (s, 1H, H-9a), 3.77 (m, 1H, 2-H_{pax}), 3.26 (m, 1H, 2-H_{peq}), 3.24 (s, 3H, OCH_3), 3.26 (m, 1H, 3-H_{peq}), 3.08 (m, 1H, 3-H_{peq}), 2.69 (m, 1H, 3-H_{pax}), 2.24, 2.23 (each s, 6H, *o*-methyl mesityl), 2.04 (s, 3H, *p*-methyl mesityl), 1.58 (s, 3H, C-6a-CH_3). ^{13}C-NMR (125.75 MHz, *DMSO*-d_6): $\delta = 188.28$ (C-6), 156.93 (C-9 or C-4a), 156.85 (C-4a or C-9), 137.44, 136.80, 135.76, 135.20 (mesityl C-2, C-4, C-6; phenyl C-1), 128.67, 128.02, 127.41, 126.71, 126.65 (mesityl C-1, C-3, C-5; phenyl C-2/6, C-3/5, C-4), 97.39 (C-5), 93.40 (C-9b), 85.60 (C-6a), 57.29 (C-9a or C-3), 56.92 (C-3 or C-9a), 53.52 (NCH_2). 48.19 (OCH_3), 45.57 (C-3), 20.62, 20.60, 19.67 (mesityl CH_3, C-6a-CH_3). MS (70 eV): *m/z* (%) = 446 [M^+] (23), 245 (60), 230 (57), 154 (41), 91 (100).

6-Benzyl-9a-methoxy-3-mesityl-9b-methyl-7,8,9a,9b-tetrahydro-3aH-1,2-oxazolo[4,5-h]-1,4-benzoxazin-4(6H)-on (**5**)

$C_{27}H_{30}N_2O_4 \cdot H_2O$ (464). Yield 12%, m.p. 228.5–230 °C. IR (KBr): $\nu = 1618\,cm^{-1}$ (CO). ^{1}H-NMR (500.13 MHz, $CDCl_3$): $\delta = 7.27$ (m, 5H, phenyl), 6.82 (s, 2H, *m*-mesityl), 5.31 (s, 1H, 5-H), 3.80 (s, 1H, 3a-H), 4.50 (m, 1H, 8-H_{pax}), 4.10 (m, 1H, 8-H_{peq}), 4.59, 4.41 (each d, 2H, CH_2-C_6H_5), 3.70 (m, 1H, 7-H_{pax}), 2.26 (m, 1H, 7-H_{peq}), 3.30 (s, 3H, OCH_3), 2.29, 2.24 (each s, 6H, *o*-methyl mesityl), 1.98 (s, 3H,

[a] *pax* = pseudo-axial, [b] *peq* = pseduo-equatorial

p-methyl mesityl), 1.62 (s, 3H, C-9b-CH_3). ^{13}C-NMR (125.75 MHz, $CDCl_3$): $\delta = 184.79$ (C-4), 157.65 (C-3 or C-5a), 157.32 (C-5a or C-3), 138.74, 134.03, 129.19, 128.75, 128.04, 126.83, 125.12 (mesityl, phenyl), 98.56 (C-5), 97.56 (C-9a), 89.73 (C-3a), 68.46 (C-9b), 61.82 (C-8), 55.09 ($NCH_2C_6H_5$), 50.24 (OCH_3), 48.09 (C-7), 21.15, 20.12, 19.81, 18.28 (mesityl CH_3, C-9b-CH_3). MS (70 eV): m/z (%) = 446 [M^+] (8), 245 (91), 230 (90), 154 (100), 135 (61), 91 (95).

4-(2-Hydroxyethyl)-9b-methoxy-6a-methyl-9-(2,4,6-trimethylphenyle)-3,4,9a,9b-tetrahydro-2H-1,2-oxazolo[5,4-h]1,4-benzoxazin-6(6aH)-one (**3c**)

Removal of the solvent left an oily residue, which crystallized on stirring with ethyl acetate. The crude product was recrystallized from a mixture of ethyl acetate and ethanol.

Yield 11%, m.p. 188–191.5 °C, UV/VIS (MeOH): λ_{max} (log ε) = 248, 307.5. IR (KBr): $\nu = 1635\,cm^{-1}$ (C=O). ^{1}H-NMR (200.13 MHz, *DMSO*-d_6: $\delta = 6.88$, 6.83 (each s, 2H, *m*-mesityl), 5.10 s (s, 1H, 5-H), 4.11 (s, 1H, 9a-H), 3.95 m (m, 1H, 2-H_{pax}), 3.45 (m, 1H, 2-H_{peq}), 3.15 (m, 3H, 3-H_{pax}, OCH_2), 3.33 (s, 3H, OCH_3), 3.15 (m, 3H, 3-H_{pax}, NCH_2), 2.74 (m, 1H, 3-H_{peq}), 2.22, 2.17, 2.03 (each s, 9H, mesityl CH_3), 1.60 s (s, 3H, C-6a-CH_3). ^{13}C-NMR (50.32 MHz, *DMSO*-d_6): $\delta = 187.96$ (C-6), 158.70 (C-9 or C-4a), 156.69 (C-4a or C-9). 135.78, 137.13 (mesityl C-2, C-4, C-6), 127.92, 127.83 (mesityl C-3, C-5), 127.20 (mesityl C-1), 95.49 (C-5), 90.36 (C-9b), 85.86 (C-6a), 63.50 (C-9a), 58.29 (C-3), 56.22 (OCH_2), 50.44 (NCH_2), 48.49 (OCH_3), 46.55 (C-3), 22.50, 20.67, 20.20, 19.58 (mesityl CH_3, C-6a-CH_3).

X-ray analysis of **5**

Crystals of **5** ($C_{27}H_{30}N_2O_4$), M = 446.55 g/mol were obtained by recrystallization from a mixture of ethanol and ethyl acetate, a specimen of size 0.3 mm × 0.5 mm × 0.5 mm was mounted at ambient temperature (298 ± 2 K) on a modified STOE – diffractometer (Mo – Kα, $\lambda = 0.71069$ Å, graphite monochromator). Cell parameters were obtained from a least squares fit to the diffractometer setting angles of 22 centred reflections with $10° \leq 2\Theta \leq 13°$. Crystal system: monoclinic, $a = 10.372$ (34) Å, $b = 11.908$ (21) Å, $c = 20.040$ (34) Å, $\beta = 97.16$ (17)°, $V = 2455.8$ (1.9) Å^3, $Z = 4$, space group $P2_1/c$, $d_c = 1.208\,g/cm^3$, $\mu = 0.08\,mm^{-1}$, F(000) = 9.52.

Diffraction data were collected for 2 octants of reciprocal space with $5.5° \leq 2\Theta \leq 60°$, $-14 \leq H \leq 14$, $0 \leq K \leq 16$, $0 \leq L \leq 28$ (ω-scans, width 1.5°, variable scan speed, between 7.5°/min and 2.5°/min), leading to a total of 7685 reflections, 7171 unique, 2260 with $I/\sigma(I) > 2$. Usual LP corrections were applied to the net intensities, 3 reflections were measured periodically, no significant deviations were observed during data collection.

The structure was solved by direct methods, all non-hydrogen atoms were found and refined with isotropic temperature factors (Minimization of $(|F_o| - |F_c|)^2$, full matrix). A difference density map was calculated, the positions of the hydrogen atoms attached to C7, C8, C11 and C13 were obtained from this map. Coordinates of all other hydrogen atoms were calculated, methyl groups were treated as rigid and a torsion angle refined for each of them. At this stage, an empirical volume- and absorption correction was applied (program DIFABS [9]). Finally, all non-hydrogen atoms were refined with anisotropic temperature coefficients. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0546$ for 361 parameters and 2260 observations (reflections with $F/(F) > 4$), $R_w = \Sigma w^{1/2}||F_o| - |F_c||/\Sigma w^{1/2}|F_o| = 0.0500$, $w = 1/\sigma^2(F)$. A final difference density map shows features up to $0.23\,e^-/Å^3$ and down to $-0.20\,e^-/Å^3$. Data Analysis was performed with programs of the SHELXTL-PLUS-system [10]. The atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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