

# Thermal and Photochemical Reactions of Naphtho[1,2,3,4-*def*]chrysenes with 4-Phenyl-1,2,4-triazoline-3,5-dione

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The thermal and photochemical reactions between naphtho[1,2,3,4-*def*]chrysenes (**1**) and 4-phenyl-1,2,4-triazoline-3,5-dione (**2**) have been compared. In the thermal reaction, **2** electrophilically attacks **1** to give substitution product **4** which in part is further transformed into **5** and **6**. In the light-induced reaction, **2** predominantly undergoes  $[4\pi + 2\pi]$  cycloaddition to **1** with subsequent loss of hydrogen to yield **6** which then photodecomposes to give a complex mixture containing **10**. **5** exists in two atropisomeric forms. The structure of one form, **5b**, was determined by X-ray crystallography.

## Thermische und photochemische Reaktionen von Naphtho[1,2,3,4-*def*]chrysen mit 4-Phenyl-1,2,4-triazolin-3,5-dion

Die thermischen und photochemischen Reaktionen von Naphtho[1,2,3,4-*def*]chrysen (**1**) mit 4-Phenyl-1,2,4-triazolin-3,5-dion (**2**) werden verglichen. In der thermischen Reaktion führt elektrophiler Angriff von **2** an **1** zum Substitutionsprodukt **4**, welches z. T. zu **5** und **6** weiter umgesetzt wird. Unter Lichteinwirkung findet vorzugsweise  $[4\pi + 2\pi]$ -Cycloaddition von **2** an **1** unter nachfolgender Dehydrierung zu **6** statt; **6** wird durch das Licht zu einem komplexen Gemisch zersetzt, aus dem **10** isoliert werden kann. **5** existiert in zwei atropisomeren Formen. Die Struktur einer dieser Formen, **5b**, wurde durch Kristallstrukturanalyse bestimmt.

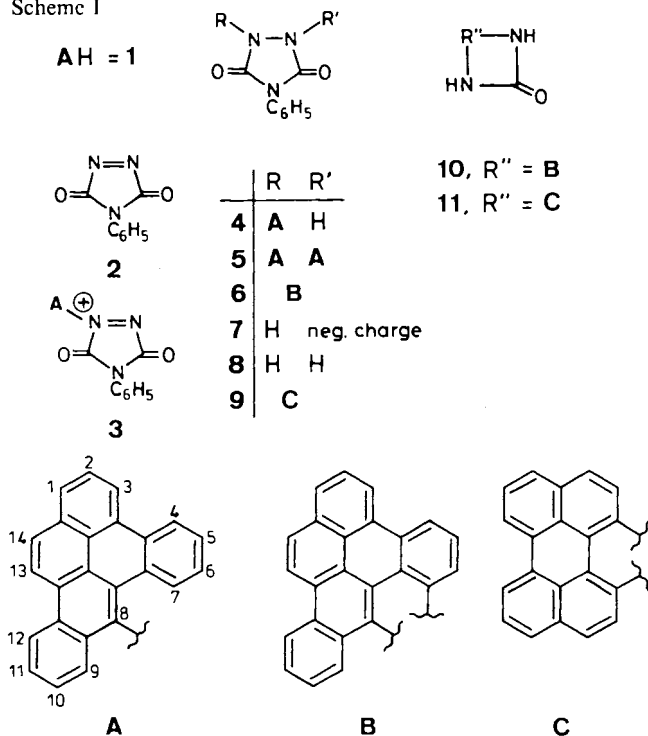
A previous report mentioned that upon thermal reaction of naphtho[1,2,3,4-*def*]chrysenes (**1**) with 4-phenyl-1,2,4-triazoline-3,5-dione (**2**), compound **4** could be readily obtained

by crystallisation from the reaction mixture<sup>1)</sup>. We now report that besides 21% of **4**, 18% of **5** and 3.5% of **6** can be isolated from the reaction mixture by chromatography.

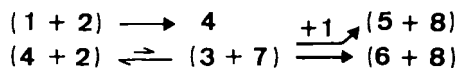
Both **5** and **6** can be prepared from **4** by the action of one mol of bromine/pyridine in dichloromethane. In the absence of **1**, this oxidation cleanly leads to **6**. This is probably the most efficient route to prepare **6**. In the presence of an excess of **1**, this oxidation predominantly leads to **5**, along with small amounts of **6**. The oxidation of **4** to **6** can also be achieved by **2** instead of bromine/pyridine, although at a much slower rate. All these oxidations proceed in the dark. All three of them can be assumed to proceed via the diazenium ion **3** which undergoes intra- or intermolecular electrophilic substitution. With bromine/pyridine as oxidant, **3** is presumably formed irreversibly from **4**, whereas with **2**, the equilibrium  $4 + 2 \rightleftharpoons 3 + 7$  certainly remains strongly on the left side; therefore, the oxidation with **2** is much slower. Its rate, however, is still comparable to the rate of formation of **4** from **1** and **2**. These observations clearly show that during the reaction of **1** with **2**, larger amounts of **5** and smaller ones of **6** have to be expected as secondary products formed from the primary product **4** by reaction with **2** and **1**. Since we observe such a product distribution, we suggest the mechanism outlined in Scheme II.

Thus, we conclude that **4** is the practically sole primary product from the thermal reaction of **1** with **2**, and is formed by electrophilic attack of **2** on the aromatic nucleus of **1**.

Scheme I

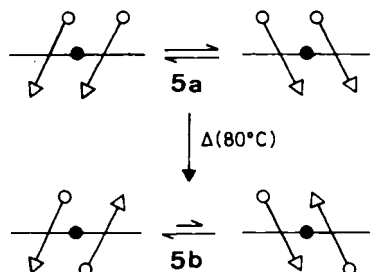


## Scheme II



From the above reactions, **5** was obtained as a mixture of two atropisomers, **5a** and **5b**, which are depicted schematically in Scheme III. Their ratio varied depending on workup conditions, but **5a** usually predominated. They could not be separated by chromatography, and since they possessed similarly low solubilities, **5a** could not be obtained pure. Heating dioxane solutions of mixtures of **5a** and **5b** resulted in virtually quantitative conversion of **5a** to **5b** which could therefore be obtained in pure condition.

## Scheme III



When **6** was irradiated with light of  $\lambda \geq 300$  nm, a complex mixture was formed from which compound **10** could be isolated by sublimation, leaving behind an intractable dark material. This reaction presumably involved light-induced cleavage of **6** to give phenyl isocyanate and dehydro-**10** which abstracted two atoms of hydrogen from the medium to yield **10**. Traces of phenyl isocyanate were detected in the reaction mixture by GLC. An analogous photoreaction has been reported previously in the case of compound **9**, which upon irradiation gave **11**<sup>2)</sup>. Irradiation of **4** and **5** also yielded complex mixtures, which, however, were quite different from those obtained from **6** and which contained neither **6** nor **10**.

When a solution of **1** and **2** was irradiated for a period sufficiently short so that thermal reaction between **1** and **2** could not compete, a mixture was obtained which resembled that obtained by irradiation of **6** (IR) and from which, too, **10** could be obtained by sublimation in comparable amount. We therefore conclude that, in contrast to the thermal reaction, the photoreaction between **1** and **2** gives predominantly **6**, which is subsequently photolysed. The mode of formation of **6** in the photoreaction must be different from that in the thermal reaction. We assume that this mode of formation is a  $[4\pi + 2\pi]$  cycloaddition within an exciplex formed from **1** and **2**, giving a Diels-Alder adduct, which is subsequently dehydrogenated; this is in accordance with our results obtained from analogous photo Diels Alder additions using maleic anhydride and other "dienophiles" in place of **2**<sup>3)</sup>.

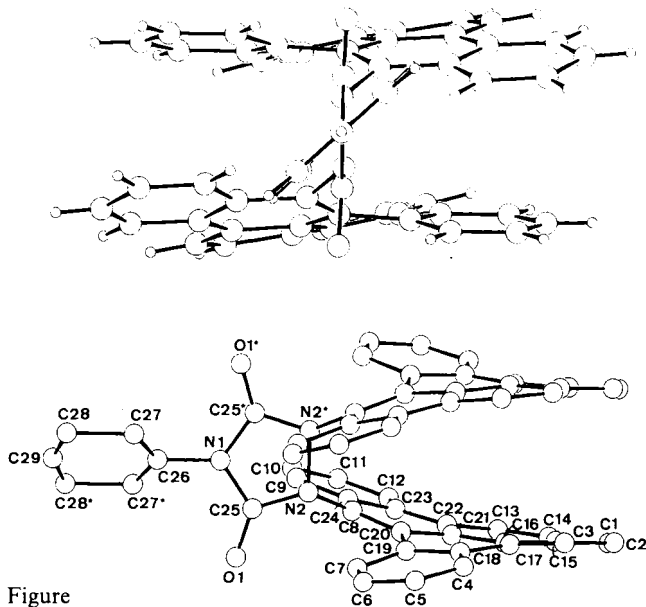
## Determination of Constitutions

The constitutions of **4** and **5b** were unequivocally confirmed by (1) the previously reported absence of the  $\gamma$ -CH vibration between 880 and 910  $\text{cm}^{-1}$  in the IR spectrum of **4**<sup>1)</sup>, (2) the <sup>1</sup>H-NMR spectrum of **4** (see Table 1 for all <sup>1</sup>H-NMR data), which shows, besides one phenyl group, the presence of two ABCD, one ABC, and one AB system, (3) the cooxidation of **1** and **4** to give **5b**, (4) the <sup>1</sup>H-NMR spectrum of **5b**, which shows, besides one phenyl group, the same systems as in **4** but their intensities doubled, thus revealing the presence of two symmetry-equivalent naphthochrysenyl moieties, and (5) the X-ray structure of **5b**. The presence of an NH band in the IR spectrum of **4** was verified by H/D exchange. The <sup>1</sup>H-NMR spectrum of **5a**, which shows the same moieties as that of **5b** but with quite different chemical shift values, and the clean conversion to **5b** on heating establish the constitution of **5a**.

The formation of **6** from **4** by loss of two hydrogen atoms and the <sup>1</sup>H-NMR spectrum of **6**, which reveals one ABCD, two ABC, one AB, and one phenyl system, show that **6** is formed from **4** by dehydrocyclisation involving either position 7 or 9 of the naphthochrysenyl moiety. Intramolecular electrophilic cyclisation of **3** (or an equivalent of **3** such as 2-bromo-**4**) should preferentially occur at position 7; this would lead to a better stabilization of the positive charge on the naphthochrysenyl moiety (in the reaction intermediate after electrophilic attack but before deprotonation) by the hydrazo-N attached to C-8.

The constitution of **10** is established by (1) its formation from **6** (by loss of phenyl isocyanate and uptake of two hydrogen atoms), (2) the <sup>1</sup>H-NMR spectrum of **10**, which shows the presence of the same systems as in **6** (except for the phenyl group), and (3) the IR spectrum showing a carbonyl band at the expected frequency as well as a NH band that was detected by H/D exchange.

The Figure shows two views of the molecule of **5b**, one approximately perpendicular to the plane of the triazoline



Figure

ring, and the other showing the exact twofold axis passing through the atoms N-1, C-26, and C-29. Atomic coordinates and interatomic distances and angles are presented in Tables 2 and 3. As can be seen in the Figure, the naphthochrysenyl groups are arranged in an approximately parallel fashion and appear to adopt a conformation which results in a large overlap between the two aromatic systems. The interaction appears to be further reinforced by a bending of the groups towards each other, which is accompanied by a simultaneous twisting of the aromatic systems. The reason for this distortion appears to be the intramolecular interaction between the two aromatic systems rather than crystal packing effects since there are no short intermolecular contacts (less than 3.0 Å) to cause such an effect. This interaction possibly explains the apparently higher stability of atropisomer **5b** compared with **5a**.

Table 1.  $^1\text{H-NMR}$  chemical shift values ( $\delta$ ) of **1**, **4**, **5**, **6**, and **10** in  $[\text{D}_6]\text{dioxane}$  and  $(\text{CD}_3)_2\text{SO}$  (in parentheses)<sup>a)</sup>

pos.	<b>1</b>	<b>4</b>	<b>5a</b>	<b>5b</b>	<b>6</b>	<b>10</b>
1	8.25	8.28	8.11	7.79 (7.81)	8.34 (8.45)	(8.28)
2	8.02	8.04	7.82	7.60 (7.67)	8.08 (8.14)	(8.06)
3	8.91	8.94	8.16	8.21 (8.08)	8.89 (9.02)	(9.12)
4	8.83	8.87	8.35	8.04 (8.06)	8.64 (8.65)	(9.02)
5	7.73	7.77	7.42	6.99 (6.99)	7.78 (7.85)	(8.04)
6	7.73	7.69	7.42	7.04 (7.04)	8.54 (8.48)	(8.33)
7	9.01	8.63	7.97	7.79 (7.86)	-	-
8	9.33	-	-	-	-	-
9	8.35	8.28	7.67	7.70 (7.74)	8.34 (8.37)	(9.27)
10	7.78	7.90	7.27	7.58 (7.74)	7.78 (7.82)	(7.95)
11	7.82	7.90	7.50	7.62 (7.67)	7.89 (7.93)	(8.01)
12	9.07	9.17	8.49	8.57 (8.70)	9.12 (9.22)	(9.27)
13	9.11	9.14	8.25	8.27 (8.41)	9.12 (9.22)	(9.27)
14	8.32	8.39	7.79	7.70 (7.86)	8.34 (8.46)	(8.63)
<i>o</i> -Ph	-	7.79	8.16	8.24 (8.16)	7.75 (7.70)	-
<i>m</i> -Ph	-	7.56	7.77	7.79 (7.87)	7.56 (7.60)	-
<i>p</i> -Ph	-	7.42	7.64	7.62 (7.74)	7.47 (7.52)	-

<sup>a)</sup> 400 MHz; all  $^3J_{\text{HH}}$  = 8–9 Hz, all  $^4J_{\text{HH}}$  = 1.5–2.0 Hz; assignments by spin-spin decoupling, except for **5a** where they are tentative.

## Experimental

UV spectra: Cary 17. — IR spectra: Perkin-Elmer 580. —  $^1\text{H-NMR}$  spectra: Bruker AM 400 — Mass spectra: Varian MAT CH 5. — Melting points: Kofler hot stage (Reichert). — Analyses: Fa. Dornis u. Kolbe, D-4330 Mülheim a.d. Ruhr.

*1,2-Bis(8-naphtho[1,2,3,4-*def*]chrysenyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (5)* and *N-Phenylbenzo[*de*]chryseno[4,5,6-*ghij*]-phthalazine-5,6-dicarboximide (6)*: A solution of 750 mg (2.5 mmol) of **1** and 270 mg (1.5 mmol) of **2** in 230 ml of dichloromethane was stirred at room temp. After 44 h, the red colour of **2** had faded. Evaporation followed by chromatography of the residue using silica gel and hexane with 0–10% of dichloromethane as eluent gave the following fractions: 327 mg of **1**, 121 mg of mixture A, 141 mg of **4** (21%, based on unrecovered **1**). Mixture A was rechromato-

graphed using silica gel and hexane/dichloromethane (2:1) as eluent: 19 mg of **6**, 44 mg of a mixture (containing 4.4 mg of **6** and 39.6 mg of **5**), and 57 mg of **5**. Chromatography can be readily monitored by UV fluorescence of the components. During attempts to dissolve **5** for recrystallization, heating was long enough for conversion to **5b** (see below; before its isomerization to **5b**, **5a** was shown to be present by  $^1\text{H NMR}$ ).

**5b**: Greenish yellow needles, mp 416–418°C. — UV (dioxane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 401 nm (3.50), 378 (3.57), 363 (3.54), 313 (sh), 297 (4.06), 275 (4.09). — IR (KBr): 1710  $\text{cm}^{-1}$ ; 1760. — MS (70 eV):  $m/z$  = 777 [ $\text{M}^+$ ].

$\text{C}_{56}\text{H}_{31}\text{N}_3\text{O}_2$  (777.9) Calcd. C 86.47 H 4.02  
Found C 85.96 H 4.10

**6**: Yellow-green needles, mp 386–388°C; solutions show a strong green fluorescence. — UV (dioxane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 426 nm (4.33), 406 (4.36), 386 (4.21), 346 (4.50), 332 (4.45), 285 (4.89), 269 (4.93), 262 (4.92), 244 (4.72). — IR (KBr): 1720  $\text{cm}^{-1}$ , 1760. — MS (70 eV):  $m/z$  (%) = 475 (60%) [ $\text{M}^+$ ], 328 (100).

$\text{C}_{52}\text{H}_{17}\text{N}_3\text{O}_2$  (475.4) Calcd. C 80.86 H 3.58 N 8.84  
Found C 80.76 H 3.69 N 8.59

*N,N'-(7,8-Naphtho[1,2,3,4-*def*]chrysendiyl)urea (10)*: A solution of 800 mg (2.6 mmol) of **1** in 700 ml of dichloromethane was placed in an irradiation apparatus (solidex glass, mercury medium-pressure lamp). With the onset of irradiation, a solution of 790 mg (5.2 mmol) of **2** in 40 ml of dichloromethane was added dropwise over a period of 20 min. After another 10 min of irradiation, the solution retained a pale pink colour. After evaporation, the residue was sublimed (1 Pa) to give 512 mg of unchanged **1** (200°C) followed by 65 mg (19% based on unrecovered **1**) of pure **10** (300°C). Yellow needles, mp 364–366°C. — UV (dioxane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 426 nm (3.76), 405 (3.83), 388 (3.80), 370 (3.68), 348 (3.82), 331 (3.82), 306 (4.28), 294 (4.30), 274 (4.38), 246 (4.30). — IR (KBr): 1655  $\text{cm}^{-1}$ ; the NH band at 3200  $\text{cm}^{-1}$  was identified by H/D exchange, which reversibly shifted it to 2320  $\text{cm}^{-1}$  (calculated: 2270  $\text{cm}^{-1}$ ). — MS (70 eV):  $m/z$  (%) = 358 (100%) [ $\text{M}^+$ ], 315 (65).

$\text{C}_{25}\text{H}_{14}\text{N}_2\text{O}$  (358.3) Calcd. C 83.81 H 3.91 N 7.82  
Found C 84.05 H 4.00 N 8.16

*Irradiation of 6*: A solution of 14 mg (0.029 mmol) of **6** in 120 ml of toluene was irradiated as before for 3.5 h. TLC showed a composition similar to the one from the previous experiment. Evaporation to 5 ml yielded 3 mg of a yellowish brown precipitate, which was sublimed to give 1 mg of pure **10** leaving behind 1 mg of a dark residue.

*Formation of 6 from 4 by Bromine/Pyridine*: To a solution of 5.17 mg (0.0108 mmol) of **4** in 8 ml of dichloromethane 0.1 ml of a solution of  $\text{Br}_2$  and pyridine (each 0.1 M) in dichloromethane was added. After several hours at 8°C in the dark, the colour of  $\text{Br}_2$  had faded and the green fluorescence of **6** appeared. After 4 d at 8°C in the dark the solution was washed with aqueous NaOH, dried with  $\text{MgSO}_4$ , and evaporated to leave 2.8 mg yellow crystals of **6**, identified by mp and  $^1\text{H NMR}$ .

*Formation of 6 from 4 by 2*: To a solution of 4.7 mg (0.0098 mmol) of **4** in 9 ml of dichloromethane a solution of 10.1 mg (0.0580 mmol) of **2** in 1 ml of dichloromethane was added. After 4 d at room temp. in the dark, the pink colour of **2** had faded. After evaporation, the residue was warmed with 1 ml of dioxane to give crystals consisting of **6** and **4** in a ratio of ca. 3:1 and a mother liquor containing predominantly **4** ( $^1\text{H NMR}$ ).

*Reaction of 4 with 1 and Bromine/Pyridine*: To a solution of 20.2 mg (0.0668 mmol) of **1** and 5.1 mg (0.0107 mmol) of **4** in 10 ml of

Table 2. Atomic fractional coordinates and equivalent isotropic thermal parameters [ $\text{\AA}^2$ ] with standard deviations in parentheses
$$U_{eq} = 1/3 \sum_i \sum_j \text{of } 5b \ U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$$

Atom	x	y	z	$U_{eq}$
O1	0.7451(4)	0.8633(4)	0.1353(5)	0.083
N1	0.8290(5)	0.8290(5)	0.0000	0.081
N2	0.6895(4)	0.7244(4)	0.0455(5)	0.048
C1	0.2335(6)	0.3502(6)	0.0885(8)	0.071
C2	0.2638(7)	0.3055(6)	0.1570(8)	0.073
C3	0.3541(6)	0.3511(6)	0.2009(7)	0.067
C4	0.5261(6)	0.4555(6)	0.3277(7)	0.067
C5	0.6052(7)	0.5089(8)	0.3891(7)	0.081
C6	0.6586(6)	0.5978(7)	0.3614(7)	0.071
C7	0.6367(5)	0.6372(5)	0.2693(6)	0.051
C8	0.5960(5)	0.6952(4)	0.0315(6)	0.044
C9	0.6336(6)	0.8136(5)	-0.1241(7)	0.063
C10	0.6072(8)	0.8523(6)	-0.2098(8)	0.081
C11	0.516(1)	0.8168(8)	-0.2352(8)	0.096
C12	0.4513(6)	0.7401(6)	-0.1780(8)	0.072
C13	0.3202(6)	0.5688(7)	-0.0637(8)	0.072
C14	0.2627(6)	0.4858(7)	-0.0234(8)	0.081
C15	0.2896(5)	0.4394(6)	0.0554(7)	0.062
C16	0.3806(5)	0.4879(5)	0.1006(6)	0.048
C17	0.4127(5)	0.4428(5)	0.1763(6)	0.052
C18	0.4996(5)	0.4918(5)	0.2329(6)	0.043
C19	0.5578(4)	0.5834(4)	0.1992(6)	0.043
C20	0.5348(4)	0.6209(4)	0.0955(5)	0.032
C21	0.4412(5)	0.5747(5)	0.0573(6)	0.045
C22	0.4139(5)	0.6156(6)	-0.0313(6)	0.051
C23	0.4755(6)	0.6976(6)	-0.0875(6)	0.054
C24	0.5684(6)	0.7357(5)	-0.0605(6)	0.053
C25	0.7549(6)	0.8118(6)	0.0682(8)	0.066
C26	0.916(1)	0.916(1)	0.0000	0.101
C27	0.9876(9)	0.9099(9)	0.009(1)	0.117
C28	1.082(1)	1.001(1)	0.012(1)	0.156
C29	1.060(1)	1.060(1)	0.0000	0.105

Table 3. Interatomic distances [ $\text{\AA}$ ] and angles [ $^\circ$ ] of **5b**.

(a) Distances				
O1 - C25	1.23 (1)	N1 - C25	1.383(9)	
N1 - C26	1.49 (2)	N2 - C8	1.43 (1)	
N2 - C25	1.38 (1)	N2 - N2*	1.452(8)	
C1 - C2	1.36 (1)	C1 - C15	1.39 (1)	
C2 - C3	1.43 (1)	C3 - C17	1.41 (1)	
C4 - C5	1.38 (1)	C4 - C18	1.41 (1)	
C5 - C6	1.37 (2)	C6 - C7	1.38 (1)	
C7 - C19	1.43 (1)	C8 - C20	1.38 (1)	
C8 - C24	1.44 (1)	C9 - C10	1.36 (1)	
C9 - C24	1.43 (1)	C10 - C11	1.39 (2)	
C11 - C12	1.38 (2)	C12 - C23	1.42 (1)	
C13 - C14	1.34 (2)	C13 - C22	1.44 (1)	
C14 - C15	1.41 (1)	C15 - C16	1.44 (1)	
C16 - C17	1.43 (1)	C16 - C21	1.41 (1)	
C17 - C18	1.44 (1)	C18 - C19	1.43 (1)	
C19 - C20	1.470(9)	C20 - C21	1.46 (1)	
C21 - C22	1.42 (1)	C22 - C23	1.42 (1)	
C23 - C24	1.42 (1)	C26 - C27	1.29 (1)	
C27 - C28	1.60 (2)	C28 - C29	1.26 (2)	
(b) Angles				
C25* - N1 - C25	110.8(8)	C26 - N1 - C25	124.6(4)	
N2* - N2 - C25	107.4(6)	N2* - N2 - C8	113.7(5)	
C25 - N2 - C8	124.3(7)	C15 - C1 - C2	121.4(9)	
C3 - C2 - C1	120.0(9)	C17 - C3 - C2	121.2(8)	
C18 - C4 - C5	120.3(9)	C6 - C5 - C4	121.2(9)	
C7 - C6 - C5	121.4(9)	C19 - C7 - C6	119.4(8)	
C24 - C8 - C20	122.0(7)	C24 - C8 - N2	119.3(6)	
C20 - C8 - N2	118.1(6)	C24 - C9 - C10	120.5(9)	
C11 - C10 - C9	120.1(9)	C12 - C11 - C10	121 (1)	
C23 - C12 - C11	121 (1)	C22 - C13 - C14	122.2(9)	
C15 - C14 - C13	122 (1)	C16 - C15 - C14	117.2(9)	
C16 - C15 - C1	119.8(8)	C14 - C15 - C1	123.0(9)	
C21 - C16 - C17	119.6(7)	C21 - C16 - C15	120.3(7)	
C17 - C16 - C15	119.5(8)	C18 - C17 - C16	120.6(8)	
C18 - C17 - C3	121.3(7)	C16 - C17 - C3	117.9(8)	
C19 - C18 - C17	118.5(6)	C19 - C18 - C4	118.7(7)	
C17 - C18 - C4	122.5(7)	C20 - C19 - C18	119.8(6)	
C20 - C19 - C7	121.4(7)	C18 - C19 - C7	118.9(6)	
C21 - C20 - C19	117.1(6)	C21 - C20 - C8	118.5(6)	
C19 - C20 - C8	121.4(6)	C22 - C21 - C20	118.8(7)	
C22 - C21 - C16	120.6(7)	C20 - C21 - C16	120.4(6)	
C23 - C22 - C21	122.1(8)	C23 - C22 - C13	121.0(8)	
C21 - C22 - C13	116.9(8)	C24 - C23 - C22	118.2(7)	
C24 - C23 - C12	117.5(8)	C22 - C23 - C12	124.0(9)	
C23 - C24 - C9	119.9(7)	C23 - C24 - C8	119.5(7)	
C9 - C24 - C8	120.6(8)	N2 - C25 - N1	107.1(7)	
N2 - C25 - O1	124.4(8)	N1 - C25 - O1	128.4(8)	
C27* - C26 - C27	128 (2)	C27 - C26 - N1	116.0(7)	
C28 - C27 - C26	118 (1)	C29 - C28 - C27	102 (1)	
C28* - C29 - C28	151 (2)			
(c) Torsion angles				
C25 - N2 - C8 - C20	-131	C25 - N2 - C8 - C24	58	
N2 - C8 - C20 - C19	16	N2 - C8 - C24 - C9	-10	
C8 - C20 - C19 - C7	23	C8 - C24 - C9 - C10	-179	
C20 - C19 - C7 - C6	-176			

dichloromethane 0.1 ml of a solution of **Br<sub>2</sub>** (0.10 M) and pyridine (0.23 M) in dichloromethane was added. After standing for 6 d at 8°C in the dark, the solution was washed with water, dried with **MgSO<sub>4</sub>**, and evaporated. Chromatography of the residue using silica gel and hexane with 0–50% of dichloromethane as eluent gave 17 mg of unchanged **1**, followed by 0.4 mg of **6**, and 7.6 mg of a 3:2 mixture of **5a** and **5b** (<sup>1</sup>H NMR).

**Isomerization of 5a to 5b:** After a part of the 3:2 mixture obtained in the above experiment had been dissolved in hot dioxane, crystals and a mother liquor were obtained upon standing at room temp. A solution of these crystals in 0.5 ml of [**D<sub>8</sub>**]dioxane in an NMR tube showed a 1:1 ratio for **5a** and **5b**. The corresponding solution of the mother liquor residue showed a 4:1 ratio for **5a** and **5b**. Heating of either NMR tube to 80°C for 48 h gave clean solutions of **5b** with no precipitates being formed. Evaporation of the solutions gave **5b**.

**X-ray Analysis of 5b:** Compound **5b** crystallizes in the trigonal space group *P*<sub>3</sub>121 with unit cell parameters *a* = 17.174(3) Å, *c* = 11.131(2) Å. Intensity data were collected from a crystal mounted in a Lindemann glass capillary on an Enraf-Nonius CAD 4 diffractometer. Crystal data and details of data collection are summarized in Table 4. The structure was solved by direct methods<sup>4)</sup>. Refinement of the structure was carried out by least-squares methods minimizing  $\sum(F_o - F_c)^2$ . The carbon atoms of the phenyl ring were poorly defined indicating some disorder of the ring. Refinement of the structure in the space group *P*<sub>3</sub> gave no significant improvement in the fit of data. The carbon atoms of the ring were refined with isotropic thermal parameters, and a peak of 0.97 e<sup>-</sup> Å<sup>-3</sup> was found 0.84 Å from C-28 in the final difference map. Hydrogen atoms were included in the refinement at calculated positions and their positional and thermal (*U<sub>H</sub>* = 0.06 Å<sup>2</sup>) parameters were not refined.

Table 4. Crystal data of **5b**<sup>5)</sup>

<b>C<sub>26</sub>H<sub>31</sub>O<sub>2</sub>N<sub>3</sub></b>	<i>Z</i> = 3
Crystal colour: yellow	Crystal size [mm]: 0.25, 0.25, 0.68
<i>M<sub>r</sub></i> = 777.9	$\lambda$ = 0.71069 Å
Trigonal	Space group: <i>P</i> <sub>3</sub> 121 (no. 152)
<i>a</i> = <i>b</i> = 17.174(3) Å	<i>R</i> = 0.087
<i>c</i> = 11.131(2) Å	Total number of reflexions: 12932 ( $\pm h, \pm k, \pm l$ )
Observed reflexions: 2275	Refined parameters: 261
[ <i>I</i> > 2σ( <i>I</i> )]	Final difference density: 0.97 eÅ <sup>-3</sup>
$\Delta\rho/\sigma$ : 0.1	$\mu(\text{Mo-K}\alpha) = 0.77 \text{ cm}^{-1}$
<i>D</i> <sub>calcd</sub> = 1.36 gcm <sup>-3</sup>	

## CAS Registry Numbers

1: 192-65-4 / 2: 4233-33-4 / 4: 55425-09-7 / **5a**: 114676-01-6 / **5b**: 114718-01-3 / 6: 114676-02-7 / 10: 114676-03-8

<sup>1)</sup> M. Zander, *Chem.-Ztg.* **99** (1975) 92.

<sup>2)</sup> M. Zander, *Chem. Ber.* **107** (1974) 1406.

<sup>3)</sup> H. Karpf, O. E. Polansky, M. Zander, *Monatsh. Chem.* **112** (1981) 659; R. Bunte, K.-D. Gundermann, J. Leitich, O. E. Polansky, M. Zander, *Chem.-Ztg.* **110** (1986) 157.

<sup>4)</sup> G. M. Sheldrick in *Crystallographic Computing 3* (G. M. Sheldrick, C. Krüger, R. Goddard, Eds.), pp. 175–189, University Press, Oxford 1985.

<sup>5)</sup> Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-52978, the names of the authors, and the journal citation.