190. A Novel Heterocyclic Ring System: Synthesis and Spectral Data of 4,8,9b-Triazacyclopenta[*c*, *d*]phenalene

by **Dongfeng Hou**[1]) and **Heinz Balli***

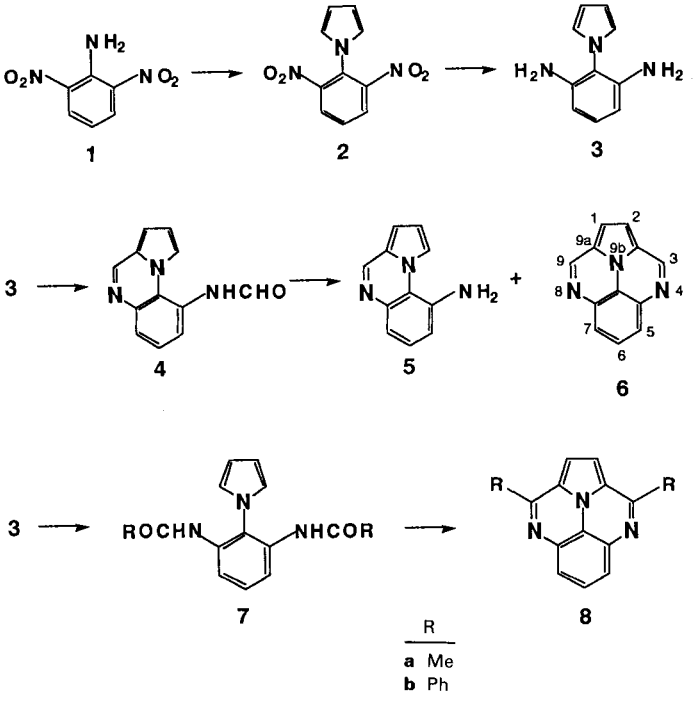
Institute of Colour Chemistry, University of Basel, St. Johanns-Vorstadt 10, CH–4056 Basel

(21.IX.92)

The synthesis and ^{1}H-NMR and electronic absorption spectra of 4,8,9b-triazacyclopenta[*c*, *d*]phenalene and several of its derivatives are described.

Heterocyclic compounds are widely used in pharmaceutical and dye chemistry, especially in the synthesis of functional dyes. Therefore, development on heterocyclic compounds of new types is currently of interest. For this purpose, we designed and synthesized the novel title compound by a four-step procedure (*Scheme 1*). Starting with

Scheme 1



[1]) Present address: Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka 591, Japan.

2,6-dinitroaniline (**1**, commercially available) and following the reaction procedure reported in [1] [2], *N*-(2,6-dinitrophenyl)pyrrole (**2**) was obtained in 20% yield by refluxing with 2,5-dimethoxytetrahydrofuran in glacial acetic acid. The reduction of **2** was achieved with hydrazine hydrate in the presence of *Raney*-Ni as catalyst, and the corresponding *N*-(2,6-diaminophenyl)pyrrole (**3**) was obtained in 72% yield.

To acylate **3**, analogous reaction conditions as reported in [3] were employed. In our case, HCOOH, Ac_2O, and benzoyl chloride were selected as acylating reagents. Acylation of **3** with HCOOH led to 9-formamidopyrrolo[1,2-*a*]quinoxaline (**4**) in 92% yield, which presumably was formed from a single ring-closure of *N*-(2,6-diformamidophenyl)-pyrrolo. The treatment of **3** with Ac_2O and benzoyl chloride gave the expected *N*,*N*'-diacyl derivatives: *N*-(2,6-diacetamidophenyl)pyrrolo (**7a**) in 75% yield and *N*-(2,6-dibenzamidophenyl)pyrrole (**7b**) in 60% yield. Polyphosphoric acid was the dehydrating reagent of choice for single ring-closure of **4** as well as double ring-closure of **7a–b**. In case of **4**, cyclization reaction afforded 4,8,9b-triazacyclopenta[*c*, *d*]phenalene (**6**) in 41% yield accompanied by 54% yield of 9-aminopyrrolo[1,2-*a*]quinoxaline (**5**) which could be converted again to **4** in nearly quantitative yield by refluxing with HCOOH. Cyclization reaction of **7a–b** afforded 3,9-dimethyl-4,8,9b-triazacyclopenta[*c*, *d*]phenalene (**8a**) in 60% yield and 3,9-diphenyl-4,8,9b-triazacyclopenta[*c*, *d*]phenalene (**8b**) in 32% yield.

The structure elucidation of **6** and **8a–b** is based upon their ^{1}H-NMR data given in *Table 1* as well as their elemental analyses, mass and IR spectra (see *Exper. Part*). In the ^{1}H-NMR spectra of **6** and **8a–b**, ring protons H–C(1) or H–C(2) *appeared* as *singlet* in the range of 7.08–7.41 ppm. In case of **6**, without substituents at H–C(3) or H–C(9) appeared as *singlet* at 9.15 ppm. The protons H–C(5), H–C(6), and H–C(7) of **6** and **8a–b** revealed an AB_2 system, which was splitted into *multiplet* in the range of 7.64–7.89 ppm.

Table 1. *360-MHz ^{1}H-NMR Data of* **6** *and* **8a–b** (δ in ppm)

Compound	H–C(1)/H–C(2)	H–C(3)/H–C(9)	H–C(5), H–C(6), and H–C(7)
6[a])	7.39	9.15	7.74–7.85 (*m*)
8a[b])	7.08	(2.78)[c])	7.64–7.76 (*m*)
8b[b])	7.41	–	7.76–7.98 (*m*)

[a]) In (D_6)DMSO. [b]) In $CDCl_3$. [c]) Me Group.

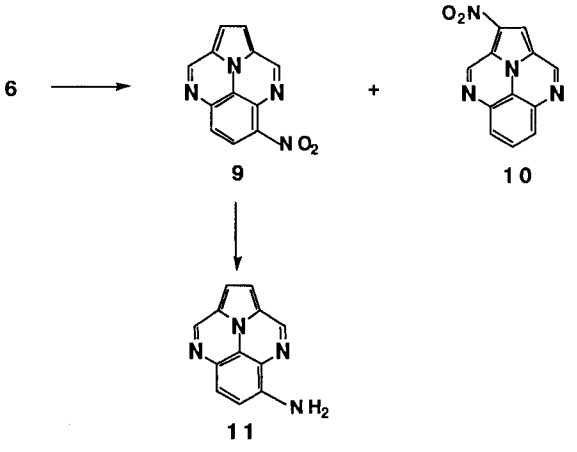
The data of electronic absorption spectra for **6** and **8a–b** are listed in *Table 2*. The UV/VIS spectrum for **6** showed eleven absorption bands with different molar exctinctions in the range of 250–480 nm, and six absorption bands for **8a** and three absorption bands for **8b** in the spectral region.

Table 2. *The UV/VIS Data of* **6** *and* **8a–b** (solvent CH_2Cl_2)

Compound	Absorption maxima [nm] (molar extinctions (log ε))
6	465 (weak), 436 (2.94), 412 (3.13), 391 (3.16), 356 (3.91), 340.5 (3.81), 326 (3.73), 315 (4.11), 302.5 (4.07), 276 (3.81), 265 (3.81)
8a	351 (3.85), 336 (3.78), 307 (4.07), 297 (4.13), 274 (3.96), 263 (3.89)
8b	373 (3.74), 329 (4.26), 274 (4.80)

To explore the development of functional dyes based upon the new heterocyclic compounds prepared, we attempted to introduce formyl group into heterocyclic ring of **6** by means of the well-known *Vilsmeier-Haack* method. But, it was unsuccessful under the reaction conditions employed. However, by using a strong electrophilic reagent, for instance, mixing acid, nitration of **6** could be achieved (*Scheme 2*). Under the reaction conditions described in our study, 5-nitro-4,8,9b-triazacyclopenta[*c*, *d*]phenalene (**9** 71% yield) and 1-nitro-4,8,9b-triazacyclopenta[*c*,*d*]phenalene (**10**, 13% yield) were obtained. Reduction of **9** with hydrazine hydrate in the presence of *Raney*-Ni as catalyst afforded 5-amino-4,8,9b-triazacyclopenta[*c*, *d*]phenalene (**11**) in excellent yield.

Scheme 2



Structure elucidation of **9**, **10**, and **11** is based upon ^{1}H-NMR data (*Table 3*) together with elemental analyses, mass and IR spectra (see *Exper. Part*). Introduction of the NO_2 group into the heterocyclic ring leads to unsymmetry of the molecule so that the differences in chemical shifts between H–C(1) and H–C(2) as well as between H–C(3) and H–C(9) are expected. In the spectra of **9** and **11**, the chemical shifts for H–C(1) and H–C(2) did not show these differences (360-MHz ^{1}H-NMR spectra), appearing as *singlet* at the same position of 7.47 ppm for **9** and 7.40 ppm for **11**, but the chemical shifts for H–C(3) and H–C(9), as expected, showed the differences of 0.03 ppm for **9** and 0.17 ppm for **11**. As for **10**, the difference of chemical shifts between H–C(3) and H–C(9) was 0.58 ppm.

Table 3. *360-MHz ^{1}H-NMR Data of* **9**, **10**, *and* **11** (δ in ppm)

Compound	H–C(1)	H–C(2)	H–C(3)	H–C(9)	H–C(5)	H–C(6)	H–C(7)
9[a])	7.47	7.47	9.39	9.36	–	8.46–8.49 (*d*)	8.00–8.02 (*d*)
10[a])	–	7.90	9.15	9.73	7.86–8.17 (*m*)[b])		
11[c])	7.40	7.40	8.54	8.71	(5.84)[d])	7.00–7.07 (*d*)	7.50–7.53 (*d*)

[a]) In (D_5)pyridine. [b]) Data for H–C(5), H–C(6), and H–C(7). [c]) In (D_6)DMSO. [d]) NH_2 Group.

Financial support by the *Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung* is gratefully acknowledged.

Experimental Part

General. Solvents and reagents were purchased from *Fluka* and *Aldrich*. M.p.: *Kofler-Mikroheiztisch* of *Leitz*; corrected. UV/VIS Spectra: *Perkin-Elmer Lambda 9* spectrophotometer; wavelengths in nm and molar extinctions in $\log\varepsilon$. IR Spectra: *Perkin-Elmer 682* spectrophotometer; absorptions in cm^{-1}. NMR Spectra: *Bruker AM-360* and *Varian VXR-400* spectrometer; chemical shifts in ppm with reference to TMS. MS: *VG70–250*; in *m/z*, relative intensity (%). Elemental analyses were performed by *Ciba-Geigy AG* and *Sandoz AG*.

N-*(2,6-Dinitrophenyl)pyrrole* (**2**). A mixture of 2,6-dinitroaniline (1.83 g, 10 mmol) and 2,5-dimethoxytetrahydrofuran (1.32 g, 10 mmol) in AcOH (30 ml) was heated under reflux for 3 h. After pouring the mixture onto ice-water (40 ml), the precipitate formed was collected, washed with H_2O, and dried in vacuum. The rough product was chromatographed on silica gel with CH_2Cl_2 and recrystallized from cyclohexane; **2** (0.47 g, 20%) as red needles. M.p. 159–161°. UV/VIS (CH_2Cl_2): 320. IR (KBr): 3130, 1610, 1580, 1540, 1505, 1360, 1325, 1080, 1020, 920, 835, 820, 755, 735, 700, 620, *etc.* ^{1}H-NMR ($CDCl_3$): 8.36–8.33 (*d*, 2H); 8.04–7.98 (*t*, 1H); 6.88–6.86 (*t*, 2H); 6.38–6.30 (*t*, 2H). MS: 233 (51, M^+), 216 (100), 170 (78), 163 (38), 140 (49), 117 (59), 83 (66). Anal. calc. for $C_{10}H_7N_3O_4$ (233.18): C 51.50, H 3.03, N 18.02, O 27.45; found: C 51.73, H 3.29, N 17.90, O 27.25.

N-*(2,6-Diaminophenyl)pyrrole* (**3**). A mixture of **2** (2.33 g, 10 mmol), hydrazine hydrate (2.5 g, 5 mmol), and *Raney*-Ni (10% based on **2**) in EtOH (10 ml) was stirred at 40°, until no more N_2 was emitted. After removing the catalyst by filtration, the filtrate was evaporated to dryness. On recrystallization from hexane, **3** (1.25 g, 72%) was obtained as off-white needles. M.p. 117–119°. UV/VIS (CH_2Cl_2): 295 (3.48). IR (KBr): 3430, 3410, 3350, 3330, 3110, 1620, 1590, 1510, 1480, 1340, 1315, 1290, 1130, 1110, 1070, 1060, 1010, 920, 780, 730, 640, *etc.* ^{1}H-NMR ((D_6)acetone): 6.9–6.8 (*t*, 1H); 6.7–6.6 (*t*, 2H); 6.3–6.2 (*t*, 2H); 6.2–6.1 (*t*, 2H). MS: 173 (100, M^+), 158 (11), 145 (24), 133 (6), 118 (11), 105 (5), 87 (7), 78 (4), 73 (2), 52 (4), 39 (6). Anal. calc. for $C_{10}H_7N_3$ (173.22): C 69.33, H 6.40, N 24.26; found: C 69.07, H 6.70, N 24.40.

9-Formamidopyrrolo[1,2-a]quinoxaline (**4**). Compound **3** (0.1 g, 0.58 mmol) in 98% HCOOH (2 ml) was heated under reflux for 1 h. After cooling, a soln. of solid NaOH (2 g) in H_2O (15 ml) was added. The precipitate formed was collected, washed with H_2O, and dried in vacuum. On recrystallization from toluene, **4** (0.11 g, 92%) was obtained as white needles. M.p. 237–238°. UV/VIS (MeOH): 335 (3.88), 246 (4.29). IR (KBr): 3200, 1660, 1615, 1590, 1530, 1475, 1450, 1425, 1390, 1340, 1320, 1280, 1240, 1190, 1155, 1040, 820, 780, 705, *etc.* ^{1}H-NMR ((D_6)DMSO): 10.53 (*s*, 1H); 8.92–8.88 (*d*, 1H); 8.62–8.32 (*m*, 2H); 7.90–7.82 (*q*, 1H); 7.54–7.38 (*m*, 2H); 7.10–6.90 (*m*, 2H). MS: 211 (58, M^+), 194 (14), 183 (100), 156 (25), 129 (7), 101 (5), 91 (7), 78 (50), 63 (9), 51 (14), 39 (15). Anal. calc. for $C_{12}H_9N_3O$ (211.22): C 68.23, H 4.30, N 19.90, O 7.57; found: C 68.1, H 4.4, N 19.8, O 7.7.

9-Aminopyrrolo[1,2-a]quinoxaline (**5**) *and 4,8,9b-Triazacyclopenta[c,d]phenalene* (**6**). To **4** (0.1 g, 0.47 mmol) was added polyphosphoric acid (PPA) (20 g) at r.t. The mixture was then heated to 160° under stirring, and then kept for 3 h. After cooling, the mixture was neutralized with 10% NaOH. The org. products were extracted with CH_2Cl_2 (3 × 30 ml). The combined extracts were dried (anh. $MgSO_4$), and then filtered. The filtrate was evaporated to leave a yellow residue (0.88 g). The residue chromatographed on silica gel with AcOEt and recrystallized from cyclohexane: **5** (0.49 g, 54%) as pale yellow needles, m.p. 147–148°, and **6** (0.38 g, 41%) as yellow needles, m.p. 235–236°, were obtained.

Data of **5**. UV/VIS (CH_2Cl_2): 360 (sh), 342 (3.87), 330 (sh), 268 (4.25), 248 (4.20). IR (KBr): 3380, 3160, 1610, 1590, 1470, 1450, 1365, 1330, 1295, 1250, 1230, 1070, 1035, 1015, 880, 830, 800, 780, 730, 675, *etc.* ^{1}H-NMR ((D_6)DMSO): 8.76 (*s*, 1H); 8.70–8.67 (*q*, 1H); 7.25–7.16 (*m*, 2H); 7.08–7.04 (*q*, 1H); 6.97–6.94 (*q*, 1H); 6.86–6.83 (*m*, 1H); 5.41 (*s*, 2H). MS: 183 (100, M^+), 156 (20), 129 (4), 118 (3), 78 (6), 63 (6), 51 (5), 39 (7). Anal. calc. for $C_{11}H_9N_3$ (183.21): C 72.12, H 4.95, N 22.93; found: C 72.11, H 5.07, N 22.82.

Data of **6**. UV/VIS (CH_2Cl_2): see *Table 2*. IR (KBr): 3120, 1630, 1605, 1600, 1515, 1450, 1415, 1350, 1340, 1305, 1265, 1235, 1210, 1115, 1050, 1035, 940, 925, 825, 815, 775, 690, *etc.* ^{1}H-NMR ((D_6)DMSO): see *Table 1*. MS: 193 (100, M^+), 165 (4), 139 (5), 97 (11), 63 (4), 39 (3). Anal. calc. for $C_{12}H_7N_3$ (193.21): C 74.60, H 3.65, N 21.75; found: C 74.59, H 3.68, N 21.83.

N-*(2,6-Diacetamidophenyl)pyrrole* (**7a**). A soln. of **3** (0.1 g, 0.58 mmol) in AcOH (15 ml) nd Ac_2O (0.4 ml) was stirred at 30° for 2 h. After adding H_2O (10 ml) to the mixture, the precipitate formed was collected, and then dried in vacuum. On recrystallization from cyclohexane, **7a** (0.11 g, 75%) was obtained as white needles. M.p. 181–182°. UV/VIS (MeOH): 223 (4.39). ^{1}H-NMR ((D_6)DMSO): 7.43–7.32 (*m*, 3H); 6.67–6.64 (*t*, 2H); 6.24–6.21 (*t*, 2H); 1.85 (*s*, 6H). MS: 257 (100, M^+), 240 (7), 214 (40), 200 (27), 172 (63), 158 (13), 145 (11), 133 (31), 118 (11), 43 (78), 39 (8). Anal. calc. for $C_{14}H_{15}N_3O_2$ (257.29): C 65.36, H 5.88, N 16.33, O 12.44; found: C 65.1, H 5.9, N 16.1, O 12.2.

N-*(2,6-Dibenzamidophenyl)pyrrole* (**7b**). To an ice-cold mixture of benzoyl chloride (0.29 g, 2 mmol) and pyridine (10 ml) was added **3** (0.173 g, 1 mmol). Then the mixture was stirred at 80° for 3 h. After the pyridine had been removed in vacuum, the residue was recrystallized from AcOEt to afford **7b** (0.23 g, 60%), which was directly used for the following cyclization reaction without further characterization.

3,9-Dimethyl-4,8,9b-triazacyclopenta[c,d]phenalene (**8a**). To **7a** (0.1 g, 0.39 mmol) was added PPA (30 g) at r.t. The mixture was heated under stirring at 160° for 4 h, and then at 180° for another 2 h. After cooling, the mixture was neutralized with 10% NaOH. The org. product was extracted with CH_2Cl_2 (2 × 10 ml). The combined extracts were dried (anh. $MgSO_4$). The solvent was evaporated to leave yellow solids. After column chromatography with AcOEt and recrystallization from cyclohexane, **8a** (52 mg, 60%) was obtained as yellow needles. M.p. 193–195°. UV/VIS (CH_2Cl_2): see *Table 2*. IR (KBr): 3120, 3030, 2920, 1605, 1600, 1515, 1430, 1400, 1380, 1370, 1360, 1325, 1315, 1250, 1160, 1060, 1040, 960, 815, 780, 705, 690, *etc.* ^{1}H-NMR ($CDCl_3$): see *Table 1*. MS: 221 (100, M^+), 206 (2), 179 (3), 153 (2), 111 (7), 75 (2), 63 (3), 51 (2), 39 (2). Anal. calc. for $C_{14}H_{11}N_3$ (221.26): C 76.00, H 5.01, N 18.99; found: C 76.04, H 5.02, N 19.14.

3,9-Diphenyl-4,8,9b-triazacyclopenta[c,d]phenalene (**8b**). To **7b** (0.1 g, 0.26 mmol) was added PPA (20 g) at r.t. The mixture was heated to 160° under stirring, and then kept for 3 h. After cooling, the mixture was neutralized with 10% NaOH. The org. product was extracted with CH_2Cl_2 (2 × 10 ml). The combined extracts were dried (anh. $MgSO_4$). The solvent was removed to leave yellow solids (65 mg). The rough product was recrystallized from AcOEt twice to give **8b** (25 mg, 32%) as yellow needles. M.p. 237–238°. IR (KBr): 3060, 1605, 1595, 1510, 1485, 1475, 1450, 1440, 1420, 1395, 1360, 1350, 1340, 1060, 1030, 890, 785, 765, 720, 700, *etc.* ^{1}H-NMR ($CDCl_3$): see *Table 1*. UV/VIS (CH_2Cl_2): see *Table 2*. MS: 345 (100, M^+), 242 (11), 173 (11). Anal. calc. for $C_{24}N_{15}N_3$ (345.41): C 83.46, H 4.38, N 12.16; found: C 83.50, H 4.37, N 12.26.

5-Nitro-4,8,9b-triazacyclopenta[c,d]phenalene (**9**) *and 1-Nitro-4,8,9b-triazacyclopenta[c,d]phenalene* (**10**). To **6** (0.35 g, 1.81 mmol) dissolved in conc. H_2SO_4 (4 ml) was added dropwise 100% fuming HNO_3 (0.16 g) at r.t. Then, the mixture was stirred at 60° for ½ h. After cooling, the mixture was neutralized with 20% NaOH. The org. product was extracted with CH_2Cl_2 (5 × 100 ml). The combined extracts were dried (anh. $MgSO_4$). The solvent was evaporated to leave yellow residue, which was washed with AcOEt to remove **10**. Then, **9** (0.31 g, 71%) was obtained as yellow solids, m.p. 286–315°. Column chromatography on silica gel with AcOEt yielded **10** (54 mg, 13%) as yellow solid, m.p. 276–277°.

Data of **9**. UV/VIS (CH_2Cl_2): 412 (4.01), 398 (4.01), 297 (3.99), 287 (3.98). IR (KBr): 3120, 3100, 3060, 1605, 1595, 1510, 1450, 1400, 1360, 1345, 1320, 1300, 1250, 1220, 1200, 1155, 1120, 1070, 1035, 940, 890, 850, 825, 815, 790, 780, 740, 690, *etc.* ^{1}H-NMR ((D_5)pyridine): see *Table 3*. MS: 238 (100, M^+), 208 (63), 192 (64), 180 (22), 165 (22), 138 (10), 88 (9), 76 (13), 63 (12), 50 (15). Anal. calc. for $C_{12}H_6N_4O_2$ (238.21): C 60.51, H 2.54, N 23.52; found: C 60.3, H 2.6, N 23.4.

Data of **10**. UV/VIS (CH_2Cl_2): 406 (3.87), 389 (3.91), 353 (3.92), 292 (4.23), 255 (3.95). IR (KBr): 3320, 3200, 1645, 1535, 1450, 1360, 1335, 1210, 1195, 1150, 1110, 1030, 825, 800, 750, 685, 620, *etc.* ^{1}H-NMR ((D_5)pyridine): see *Table 3*. MS: 238 (100, M^+), 208 (15), 192 (76), 165 (4), 138 (8), 88 (5), 75 (7), 64 (8), 50 (6). Anal. calc. for $C_{12}H_6N_4O_2$(238.21): C 60.51, H 2.54, N 23.52; found: C 60.4, H 2.8, N 23.4.

5-Amino-4,8,9b-triazacyclopenta[c,d]phenalene (**11**). A mixture of **9** (0.31 g, 1.3 mmol), hydrazine hydrate (0.2 g, 4 mmol), and *Raney*-Ni (20% based on **9**) in EtOH (150 ml) was stirred at 50°, until no more N_2 was emitted. The mixture was filtered to remove the catalyst. The filtrate was evaporated to leave **11** (0.27 g, 98%) as red powder. M.p. 245–247°. UV/VIS (CH_2Cl_2): 443 (2.66), 373 (3.90), 356 (3.90), 339 (3.80), 322 (3.96), 312 (3.97), 276 (3.71), 243 (4.56). IR (KBr): 3320, 3200, 1645, 1535, 1450, 1360, 1330, 1210, 1195, 1150, 1110, 1030, 825, 795, 750, 685, 620, *etc.* ^{1}H-NMR ((D_6)DMSO): see *Table 3*. MS: 208 (100, M^+), 180 (15), 104 (7), 90 (6), 57 (3), 43 (3).

REFERENCES

[1] N. Elming, N. Clauson-Kaas, *Acta Chem. Scand.* **1952**, *6*, 867.
[2] S. Vomero, F. Chimenti, R. Giuliano, M. Artico, *Farmaco, Ed. Sci.* **1976**, *31*, 681.
[3] G. W. H. Cheeseman, B. Tuck, *J. Chem. Soc. (C)* **1966**, 852.