

CONFORMATIONAL STUDIES ON HELICENES—VIII¹

SYNTHESIS AND CONFORMATION OF TWO HEXAHELICENE ANALOGUES HAVING A NON-AROMATIC, FIVE-MEMBERED RING

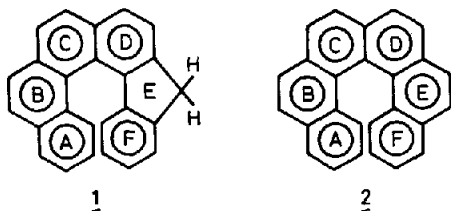
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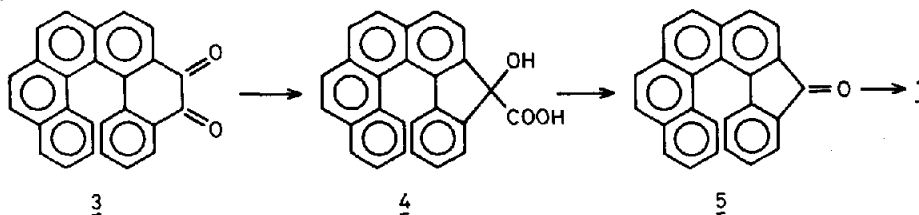
Abstract—Phenanthro[3,4-c]fluorenone (5) and phenanthro[3,4-c]fluorene (1) have been prepared from hexahelicene-5,6-quinone. The effect of the presence of a five-membered ring on the helical conformation has been studied by comparison of NMR data of 1 and 5 with those of hexahelicene. Force field calculations of the structure of 1 agree with the results of the NMR analysis.

In our study on hexahelicenes, in which one of the benzene rings has been replaced by another ring system, we reported in the previous paper¹ the synthesis, the spectral properties and a conformational analysis of 5,6-dihydrohexahelicene. In this paper a similar study of phenanthro[3,4-c]fluorene (1) is described, in which the penultimate ring (E) of hexahelicene (2) has been replaced by a cyclopentadiene ring. The compound (1) is also of interest because it can be converted into a fully aromatic anion by treatment with alkali metals, as has been done with indene and fluorene itself.² This will be the subject of a subsequent paper.³



A trivial method for the preparation of 1 might be the photodehydrocyclization of 1-(2-naphthyl)-2-(3-fluorenyl)ethylene, but 3-fluorenyl derivatives are difficult of access and the preference of photocyclization of the ethylene is certainly to the less hindered side. From several other possibilities we chose the recently described⁴ hexahelicene quinone (3) as the starting compound for the synthesis of 1. Ring contraction by a benzilic acid rearrangement, followed by reduction of the keto group in the resulting cyclopentadienone ring would lead to the desired compound (Scheme 1). Although the

Scheme 1



very old method of Anschütz,⁵ using sodium hydroxide and potassium permanganate for the benzilic acid rearrangement, and subsequent oxidation converted phenanthroquinone into fluorenone in a yield of more

than 90%, application of this method to 3 yielded only 10–20% of 5. Because of the low solubility of 3 in aqueous solutions we repeated the reaction in a two phase system (dichloroethane/water) in the presence of *tert* butylammonium chloride, but the yield did not increase. Application of a concentrated sodium hydroxide solution also did not improve the yield of 5 nor that of the α -hydroxy acid 4, which may be the main product under these circumstances.⁶ However, when the reaction was carried out in a homogeneous solution of 3 in a mixture of dioxane and water, the ketone 5 could be isolated in more than 50% yield. This product was identified by IR: C=O (stretch) 1705 cm⁻¹ (KBr) (fluorenone 1710 cm⁻¹, hexahelicene-quinone 1670 cm⁻¹) and by mass spectroscopy: *m/e* (peak matching) 330.1052 \pm 0.003, calc for C₂₅H₁₄O 330.1045.

Wolff-Kishner reduction of 5 gave 1 in 65% yield.

NMR spectra of 1 and 5

The NMR spectra of 1 and 5 measured in CDCl₃ are reproduced in Fig. 1. For the assignment of the absorptions use was made of the analogy of spectra of related compounds and of decoupling experiments.

In Table 1, δ -values of all protons in the compounds 1, 2 and 5, measured in CDCl₃ as well as C₆D₆, are given and compared with those of fluorene (7) phenanthrene (8) and fluorenone (6), which represent the moiety DEF of the helicenes investigated. It is clear that the differences of δ -values ($\Delta\delta$) of the corresponding protons A', B', C', D' in the compounds 5, 1 and 2 are caused by the different structure of ring E as well as by conformational differences of the respective helical compounds. In order to analyse the conformational differences between the

compounds 5, 1 and 2 we suppose that $\Delta\delta$ -values of the protons A'-D' caused by the presence of different neighbouring rings in this series of compounds are nearly equal to those in the series of corresponding compounds

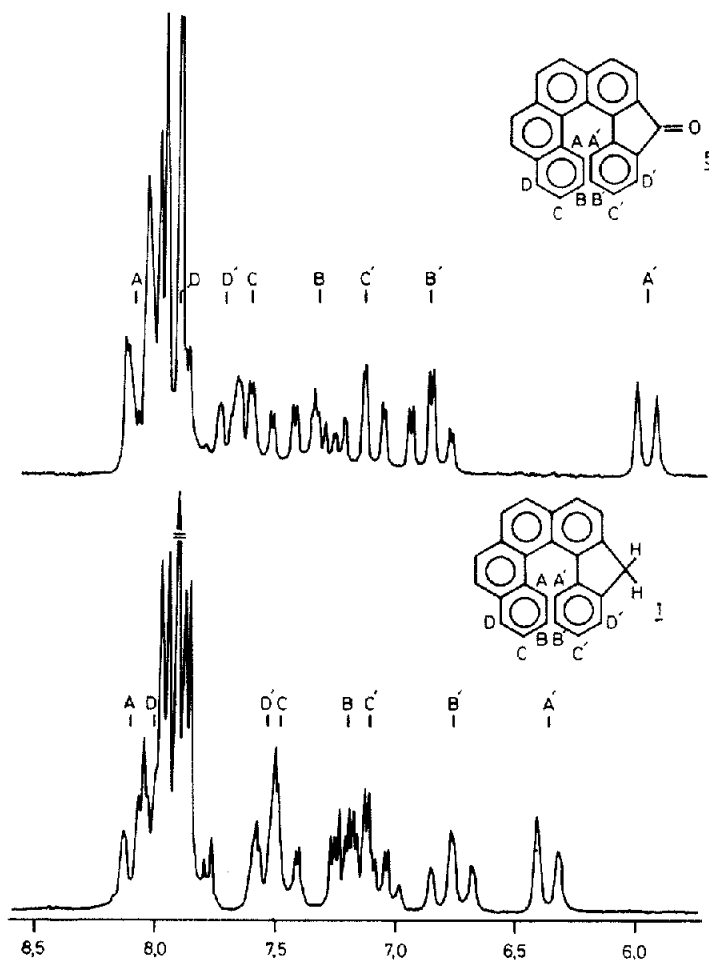


Fig. 1. NMR spectra of 5 and 1 in CDCl_3 at 90 MHz.

6, 7 and 8. Thus, for the conformational analysis we compare $\Delta\delta$ -values for 2 and 5, 2 and 1, and 1 and 5, with $\Delta\delta$ -values for 8 and 6, 8 and 7, and 7 and 6, respectively. These $\Delta\delta$ -values are given in Table 2.

The data for the compounds 1 and 5 show that the conformations of these compounds must be very equal. In the non-associating solvent CDCl_3 $\Delta\delta$ -values of the protons A-D (ring A) are small (<0.15 cps). In ring F a larger $\Delta\delta$ -value is found for proton A', but is nearly equal to that of the corresponding 7 and 6; for the protons B'-D' just as low $\Delta\delta$ -values are found for 1 and 5 as for 7 and 6. The data for the protons A'-D' suggest that the rings E and F in 1 and 5 are nearly coplanar as they are in 6 and 7, so that the distance between opposite rings in the helical compounds 1 and 5 will be larger than in 2, in which the coplanarity between the rings E and F is much more disturbed.

This conclusion is consolidated by the $\Delta\delta$ -values for the protons A-D in 2 and 5, and 1 and 5. The protons C and D in 1 and 5 appear to be less shielded by the opposite ring F than in 2; in fact the δ -values of these protons do not deviate much from those of the corresponding protons in phenanthrene 8. Similarly, proton B in 1 and 5 is shifted downfield compared to 2. The enhanced effect, relative to the protons C and D, must be ascribed to the absence of a ring current in the opposite ring F in 1 and 5. The absence of a shielding influence of this ring in these compounds should cause an even larger

downfield shift for proton A, compared to 2, but for this proton the expected effect is reduced by the diminished van der Waals interaction between protons A and the opposite rings.

At the opposite side of the helix (ring F) $\Delta\delta$ -values for the protons D', C' and B' are smaller for 2 and 5, and for 2 and 1 than for 8 and 6, and 8 and 7, respectively. The differences increase in the order $D' < C' < B'$. This points again to more shielding of these protons by opposite rings in 2 than in 1 and 5. The position of the A' proton in 1 and 5 is at remarkably high field. Apparently, the shielding effect of the opposite, aromatic ring B is much less balanced by the downfield effect, due to van der Waals interaction, than in 2, because of a larger distance between the ends of the helix.

The methylene group of 1 appears as an AB pattern in the NMR spectrum, what is not the case with 7. The proton at lower field ($\delta 4.39$) must be that nearer to the opposite rings, because it lies in the deshielding zone of these rings. The coupling constant ($J = 22.5$ Hz) is in good accordance with that given for 7 ($J = 21.0$ Hz).⁷

The δ - and $\Delta\delta$ -values, measured in C_6D_6 are less suitable for the conformational analysis as a consequence of differences in association with this solvent. The aromatic solvent induced shifts (ASIS effect) of 1 and 2 are rather equal for all protons in the terminal rings with the exception of D', which is nearest to the methylene group in 2. The ASIS effect of 1 and 5 (or 2 and 5)

Table 1. δ -Values (ppm) of protons in 1, 2 and 5 and of the related compounds phenanthrene (8), fluorene (7) and fluorenone (6), measured in CDCl_3 and C_6D_6

Compound	5			1			2		
	CDCl_3	C_6D_6	ASIS-effect ($\delta_{\text{CDCl}_3} - \delta_{\text{C}_6\text{D}_6}$)	CDCl_3	C_6D_6	ASIS-effect	CDCl_3	C_6D_6	ASIS-effect
A	8.04	7.95	0.09	8.08	8.34	-0.26	7.58	7.83	-0.25
B	7.32	6.99	0.33	7.17	7.00	0.17	6.65	6.52	0.13
C	7.58	7.26	0.32	7.50	7.28	0.22	7.18	7.00	0.18
D	7.90	7.73	0.17	8.02	7.83	0.19	7.78	7.63	0.15
E							7.87	7.69	0.18
F							7.87	7.69	0.18
G	7.88- 8.03	7.34- 7.78		7.77- 8.06	7.62- 7.87		7.92	7.72	0.20
H							7.92	7.72	0.20
H'	7.91	7.33	0.58	7.58	7.54		7.92	7.72	0.20
G'	8.05	7.96	0.09		7.69		7.92	7.72	0.20
F'	-	-		-	-		7.87	7.69	0.18
E'	-	-		-	-		7.87	7.69	0.18
D'	7.67	7.53	0.14	7.55	7.24	0.31	7.78	7.63	0.15
C'	7.11	6.64	0.47	7.12	7.01	0.11	7.18	7.00	0.18
B'	6.83	6.40	0.43	6.77	6.72	0.05	6.65	6.52	0.13
A'	5.93	5.91	0.02	6.38	6.68	-0.30	7.58	7.83	-0.25
CH_2	-	-		4.39 4.02	4.00 3.57	0.39 0.45			
				$J_{\text{CH}_2} -22.5 \text{ } -22.1\text{Hz}$					
Compound	6			7			8		
A'	7.38	6.72- 7.02		7.79	7.68	0.11	8.65	8.44	0.21
B'	7.38			7.37	7.25	0.12	7.61	7.39	0.22
C'	7.20		7.29	7.25	0.04	7.57	7.36	0.21	
D'	7.57	7.59	-0.02	7.53	7.58	-0.05	7.86	7.65	0.21
CH_2				3.91	3.46	0.46			

Table 2. Differences in chemical shifts ($\Delta\delta$) of corresponding protons of the compounds 1, 2 and 5, and 6, 7 and 8.

Proton	Solvent CDCl_3					
	$\Delta\delta$ 2-5	8-6	2-1	8-7	1-5	7-6
A	-0.46		-0.50		0.04	
B	-0.67		-0.52		-0.15	
C	-0.40		-0.32		-0.08	
D	-0.12		-0.24		0.12	
D'	0.11	0.29	0.23	0.33	-0.12	-0.04
C'	0.07	0.37	0.06	0.28	0.01	0.09
B'	-0.18	0.23	-0.12	0.24	-0.06	-0.01
A'	1.65	1.27	1.20	0.86	0.45	0.41
	Solvent C_6D_6					
A	-0.12		-0.51		0.39	
B	-0.47		-0.48		0.01	
C	-0.26		-0.28		0.02	
D	-0.10		-0.20		0.10	
D'	0.10	0.06	0.39	0.07	-0.29	-0.01
C'	0.36		-0.01	0.11	0.37	
B'	0.12		-0.20	0.14	0.32	
A'	1.92		1.15	0.76	0.77	

are rather different, especially for proton A and for the protons A', B' and C' in ring F. In **1** and **2** benzene can only associate with the rings, but in **5** the carbonyl group, pointing with its positive end to the centre of the benzene nucleus strongly contributes to the association.

Conformation of **1**, calculated by the force-field method

The qualitative picture of the conformational differences between **1** (and **5**) and **2**, derived from NMR data, has been checked by a force-field calculation of the conformation of **1**. We used the Warshel programme, which has given previously very reliable results for other helicenes.⁸ In Fig. 2 two projections of the calculated structure of **1** are compared with those of the structure of **2**, calculated in the same way. In Table 3 relevant distances of both compounds are given.

Carbon atoms and rings in **1** have been indexed correspondingly to those in **2** (see Fig. 3).

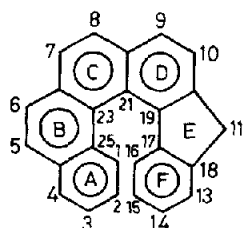


Fig. 3. Indexing of C atoms and rings in **1**.

The data consolidate the main conclusion of the NMR analysis: the right end of **1**, containing the rings E and F, is more planar than in **2**. This appears from the smaller torsion angles for the inner bonds C(21)-C(19) and especially C(19)-C(17) in **1**, whereas the torsion angles for C(25)-C(23) and C(23)-C(21) are equal to those in **2**. The coplanarity of the rings E and F is also apparent from the torsion angles of the bonds C(17)-C(18) and C(11)-C(18), which are near to 180°.

The larger distance between opposite ends of the helical structure of **1** in comparison with **2** is at least partly due to shifting-away of ring F from A and B, as is illustrated in projection a in Fig. 2: the presence of the

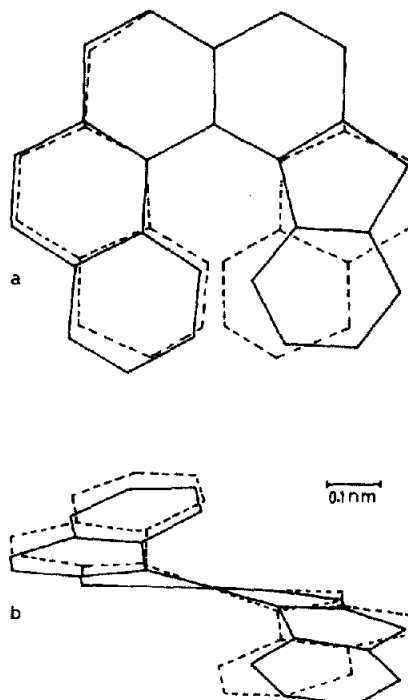


Fig. 2. Projections of the calculated structure of **1** (—) and **2** (---). (a) Projection on a plane perpendicular to an axis perpendicular to the C²¹-C²² bond. (b) Projection on a plane perpendicular to the axis through C²¹-C²².

five-membered ring enlarges the distance C(16)-C(21). By this effect C(1) is nearer to C(16) than to C(17) in **1**, whereas it is nearer to C(17) than to C(16) in **2**; this consequence of the structural difference is also visible in the nearly equal distances C(1)-C(19), H(1)-C(17) and H(1)-C(19) in both compounds and the larger differences found for C(2)-C(15) and H(16)-C(23); the proton H(16) is nearer to C(25) than to C(23) in **1**, but nearer to C(23) than to C(25) in **2**. It deserves attention that the distance between H(1) and the centre of the opposite ring E is

Table 3. Molecular parameters of compounds **1** and **2**, calculated by the force-field method

	1	2	
bonding distances (nm)	inner helix:	0.145	0.146
non-bonding distances (nm):	C(1)-C(16)	0.304	0.311
	C(1)-C(17)	0.309	0.301
	C(1)-C(19)	0.314	0.312
	C(2)-C(15)	0.427	0.411
	H(1)-C(17)	0.264	0.263
	H(1)-C(19)	0.255	0.250
	H(16)-C(23)	0.294	0.250
	H(16)-C(25)	0.258	0.263
other distances (nm)	H(1) - centre of ring E	0.353	0.338
	H(16) - centre of ring B	0.297	0.338
torsion angles (°)	C(1)-C(25)-C(23)-C(29)	15.9	15.7
	C(25)-C(23)-C(21)-C(19)	26.9	26.6
	C(23)-C(21)-C(19)-C(17)	23.4	26.6
	C(21)-C(19)-C(17)-C(16)	5.4	15.7
	C(16)-C(17)-C(18)-C(11)	187.9	
	C(21)-C(19)-C(20)-C(11)	181.7	
	C(19)-C(20)-C(11)-C(18)	164.4	
	C(20)-C(11)-C(18)-C(13)	188.6	
angles between least square planes through rings (°):	AB	9.8	9.2
	BC	12.3	12.3
	CD	11.2	12.9
	DE	14.4	12.3
	EF	7.0	9.2
	FA	50.1	41.1

Table 4. δ -Values of protons in **1**, **9** and **10**, measured in CDCl_3

Protons	9	10	1
A	7.88	7.94	8.08
B	6.88	6.85	7.17
C	7.19	7.16	7.50
D	7.65	7.69	8.02
D'	7.46 ^a	7.18	7.55
C'	6.94 ^a	6.80	7.12
B'	6.44 ^a	6.31	6.77
A'	6.04 ^a	6.26	6.38

a) Values at -40°C ; at room temperature one broad signal centered at 6.95 ppm is observed

larger, but the distance between H(16) and the centre of the ring B is smaller in **1** than in **2**. This may explain the strong shielding of the protons.

In Table 4 the enlargement of the distance between the terminal rings in **1** as a consequence of the presence of a 5-membered ring is illustrated in another way, by comparison of NMR data of **1** with those of two other compounds which have no ring current in ring E, viz. 1-phenylbenzo[c]phenanthrene¹ (**9**), in which ring E is completely absent and 5,6-dihydrohexahelicene¹ (**10**), in which ring F is partly saturated.

It appears that δ -values of corresponding protons in **9** and **10** show only small differences. All protons in **1**, however, absorb at lower field than corresponding protons in **9** and **10**.

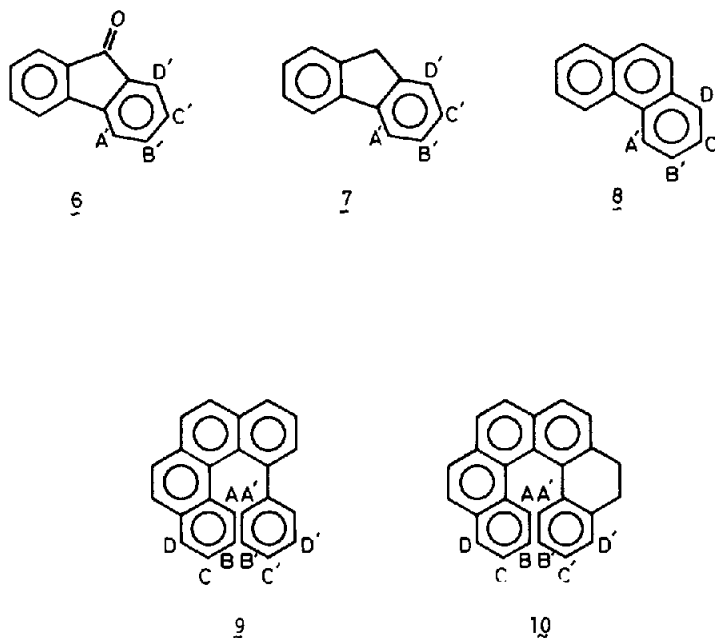
The NMR spectrum of **1** measured in $\text{C}_6\text{D}_5\text{NO}_2$ at 190° was unchanged, no trace of a broadening of the AB pattern of the CH_2 group could be observed. This implies that no racemization of **1** occurs below this temperature; ΔG_{rac}^* must be higher than $100 \text{ kJ} \cdot \text{mol}^{-1}$ ($24 \text{ kcal} \cdot \text{mol}^{-1}$). (For **2** $\Delta G_{\text{rac}}^* = 146.2$; **10** $> 100 \text{ kJ} \cdot \text{mol}^{-1}$, for a derivative of **9** $\Delta G^* = 67 \text{ kJ} \cdot \text{mol}^{-1}$).

EXPERIMENTAL

NMR spectra were measured using a Bruker W.H. 90 spectrometer. δ -Values are relative to TMS. Mass spectra were obtained using a Varian SM I-B spectrometer. Hexahelicene quinone (**3**) was prepared as described previously.⁴

Phenanthro[3,4-c]fluorenone (**5**). The best way to prepare (**5**) was: hexahelicene quinone (500 mg) was dissolved in 70 ml of a dioxane/water mixture (1:1) and 2.5 g of NaOH was added to the solution. The solution was heated at 100° . After 24 h 2 g NaOH was added and the solution was heated again for 4 days. The reaction mixture was then cooled, acidified with hydrochloric acid and extracted with CH_2Cl_2 . The extract was washed with water and dried over MgSO_4 . After evaporation of the solvent the residue was chromatographed over silica. The ketone and quinone could be separated by elution with a mixture of hexane and chloroform (9:1). The yield of the ketone was 52%. After crystallization from ethyl acetate m.p. $204\text{--}207^\circ$. IR(KBr) 1710 cm^{-1} (C=O). NMR: see Table 1. MS 330.1052 ± 0.003 calcd for $\text{C}_{25}\text{H}_{14}\text{O}$: 330.1045; m/e (%; fragment): 330(100), 315(12), 300(24; $\text{M}^+ - \text{CH}_2\text{O}$), 231(16), 228(11), 206(15), 200(10).

Phenanthro[3,4-c]fluorene (**1**). **3** (50 mg), NaOH (120 mg), triglycol (18 ml) and hydrazine (3 ml) were refluxed at 130° for 2 h and another 2 h at 160° . The yellow solution was extracted with ether and water. The ether layer was washed with dil. HCl and water, dried over MgSO_4 and evaporated. The residue was



chromatographed on silica and eluted with hexane/chloroform (19:1). Yield: 30 mg. m.p. 185–188°. NMR: see Table 1. MS 316.1273 ± 0.003, calc. for C₂₅H₁₆: 316.1252; *m/e* (%): 316(100), 315(39), 314(20), 313(35), 301(12), 300(12).

REFERENCES

- ¹Previous paper in this series: J. H. Borkent, J. W. Diesveld and W. H. Laarhoven, *Recl. Trav. Chim. Pays Bas* **100**, 114 (1981).
²D. Hellwinkel and G. Haas, *Justus Liebigs Ann. Chem.* 145 (1979); see also J. van der Kooy, Thesis, Amsterdam (1971).
³Corresponding dianions, derived from hexahelicenes having a cyclopentadienyl ring at both sides of the helix might be interesting precursors of polymeric metallocenes. See F. J. Katz and W. Stusarek, *J. Am. Chem. Soc.* **101**, 4259 (1979).
⁴J. W. Diesveld, J. H. Borkent and W. H. Laarhoven, *Recl. Trav. Chim. Pays Bas* **99**, 391 (1980).
⁵R. Anschütz and F. R. Japp, *Ber.* **11**, 211 (1878); see also G. E. Inglett and F. F. Smith, *J. Am. Chem. Soc.* **72**, 842 (1950) and M. V. Bhatt, *Tetrahedron* **20**, 803 (1964).
⁶P. Fiedländer, *Ber.* **10**, 534 (1877).
⁷H. Günther, *NMR-Spectroscopic*. Georg Thieme Verlag, Stuttgart (1974).
⁸J. B. M. Somers, J. H. Borkent and W. H. Laarhoven, *Recl. Trav. Chim. Pays Bas* **100**, 110 (1981).