57. Propellanes. LXII. The *Endo*- and *Exo*-Adducts of 11-Cyano-1,6-methano[10]annulene with 4-Methyl-1,2,4-triazoline-3,5-dione[1])

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Dedicated to the memory of Professor *Frantisek Šorm*

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Summary

The title compounds have been isolated and their structures determined by X-ray crystallography. Their relative stability is discussed in terms of theory and experiment. The *endo*-adduct is the thermodynamically more stable one.

We have prepared many *Diels-Alder* adducts of propellanes and of bridged [10]annulenes with *N*-methyl- and *N*-phenyl-triazolinedione [2]. Although we were aware of the potential existence of configurational isomers of the *Alder endo*- and *exo*-type we have only now come across such a set, **1** and **2**, resulting from the reaction of 11-cyano-1,6-methano[10]annulene and 4-methyl-1,2,4-triazoline-3,5-dione (MTAD). The *endo*-isomer (**1**) is the thermodynamically more stable one and forms yellowish prisms whilst the *exo*-isomer (**2**) was obtained as thin transparent colorless plates. The triazolidinedione ring in each case is *anti* both to the cyclopropane bridge and to its cyanosubstituent, as determined by X-ray crystallography. ORTEP projections of **1** and **2** are given in *Figures 1* and *2*, respectively.

Although *N*-inversion barriers have been studied extensively, we are aware of studies on amines and hydrazines but we have found no data regarding those of cyclic hydrazides, in general, or this functionality in a 1,2,4-triazolidinedione ring, in particular. *Nelsen*'s work on polycyclic hydrazines shows inversion barriers of 12-15 kcal · mol^{-1}, attributed to lone-pair/lone-pair interactions in the inversion transition state [3]. It is reasonably believed that conjugation of the *N*-lone pair with a carbonyl group stabilizes planarity at the *N*-atoms, lowering the inversion barrier [4].

MNDO and *ab initio* STO-3G calculations for suitable models more relevant to the behaviour of **1** and **2** for both consecutive *N*-inversion with a half-planar transition state at the *N*-atoms and for simultaneous double *N*-inversion with a doubly planar transition state have been carried out [5].

These calculations and additional considerations and explications [5] lead to the prediction that the inversion of **2** to **1** would cost *ca.* 7 kcal · mol^{-1} (and of **1** to **2** *ca.* 9 kcal · mol^{-1}).

It is, of course, possible to consider the expression **3** for the inversion concerned.

In the case of the pair **1** and **2**, despite the fact that **1** is the thermodynamically more stable, **2** crystallizes out as a kinetic product despite the rapid equilibrium $\mathbf{1} \rightleftharpoons \mathbf{2}$, enabling us to obtain the structures in *Figures 1* and *2* [6].

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[1]) Part LXI: see [1].

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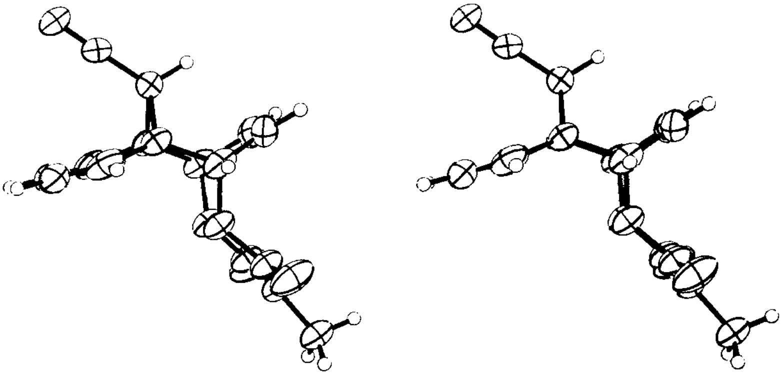


Fig. 1. *ORTEP projection of compound* **1**

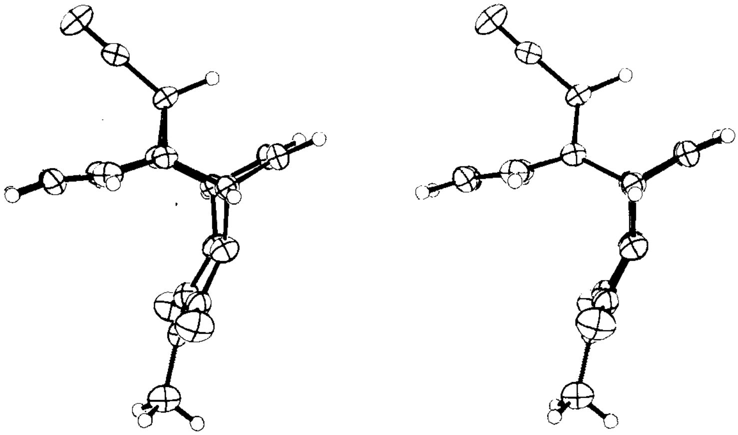
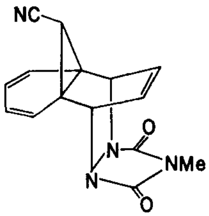


Fig. 2. *ORTEP projection of compound* **2**



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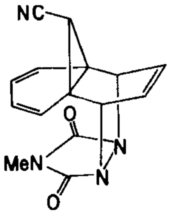

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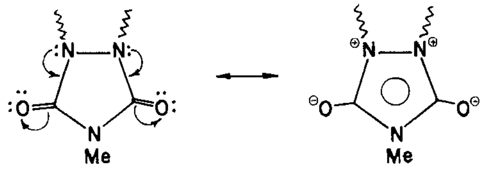

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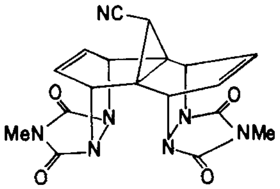

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The calculations are consistent with the fact that the RT. to $-30°$ ^1H- and ^{13}C-NMR. spectra of both isomers in solution were identical. Isomerization in the solid state, however, must overcome strong crystal packing forces: isomer **1** melts at 190-191°; isomer **2** sinters at *ca.* 175° and then melts at 190-191°, having been converted into **1**. The powder patterns of **1** and **2** were obtained at RT. using a *Debye-Scherrer* camera. After heating of **2** to 175° and cooling to RT., its powder pattern is identical to that of **1** indicating that the transformation $\mathbf{2} \rightarrow \mathbf{1}$ has indeed taken place at *ca.* 190°.

It is also not surprising that **1** and **2** do not maintain their configurational integrity when each is treated with another equivalent of MTAD. The same *bis*-adduct **4** is obtained, in which each ring originating from the dienophile has the *endo*-configuration, each is *anti* to the cyclopropane ring but this time, of course, one is *anti* to its cyano substituent as in both **1** and **2**, but the other is *syn* to it.

We are grateful to Prof. *E. Vogel* of Köln for making available to us the 11-cyano-1,6-methano-[10]annulene which we used in this work (*cf.* [7]).

Experimental Part

Diels-Alder *addition*. To the solution of the annulene (120 mg) in CH_2Cl_2 (20 ml) at RT. was added MTAD (82 mg) and the whole was stirred magnetically until disappearance of the color (2 h). Removal of the solvent gave the mono-adduct (190 mg). Crystallization of a portion of the solid residue from $CHCl_3$ gave thin transparent plates of **2**, m.p. 190-191° (sint. 175°). Crystallization of another portion from benzene gave yellowish prisms of **1**, m.p. 190-191° and transparent prisms of same m.p. which turned out (by X-ray crystallography) to consist of $\mathbf{1} \cdot 1\ C_6H_6$. Crystallization from C_6H_6/C_6H_{14} gave pure **1**, m.p. 190-191°. - IR. ($CHCl_3$): 1780, 1720, 1450, 1380 cm^{-1}. - ^1H-NMR. ($CDCl_3$): 6.7-6.0 (*m*, 6 vinylic H); 5.2 (*t*, 2 CHN); 2.95 (*s*, 3 NCH_3); 2.4 (*s*, 1 cyclopropyl H). - ^{13}C-NMR. ($CDCl_3$): 5.7 (CHCN); 26.0 (NCH_3); 30.0 (quat. C); 57.1 (CHN); 121.2, 125.5, 127.7 and 129.6 (vinylic C and CN); 158.7 (CO). - MS.: 280 (7); 166 (100); 153 (17); 140 (22).

$C_{15}H_{12}N_4O_2$ (280.0961) Calc. C 64.27 H 4.32 N 19.99% Found C 64.12 H 4.38 N 19.85%

Bis-adduct **4**. This was prepared either from **1** (16 mg) and MTAD (6.5 mg) in CH_2Cl_2 (5 ml), from **2** (21 mg) and MTAD (8.5 mg) in CH_2Cl_2 (5 ml) or from the annulene (171 mg), MTAD (228 mg) in CH_2Cl_2 (10 ml) with stirring for 7 days. In the last reaction annulene (39 mg) was recovered, mono-adducts **1** (123 mg) and *bis*-adduct (118 mg) were obtained. The *bis*-adduct had m.p. 212-213° (CH_3CN). - IR. (KBr): 2250, 1770, 1710, 1370 cm^{-1}. - ^1H-NMR. ($CDCl_3$): 6.6-6.0 (*m*, 4 vinylic H); 5.7-5.3 (*m*, 4 CHN); 2.95 (*s*, 6 NCH_3); 2.3 (*s*, 1 cyclopropyl H). - MS.: 393 (4.5); 280 (7); 198 (100); 166 (53); 153 (52); 141 (33). Calc. for $C_{18}H_{15}N_7O_4$ 393.1184, Found 393.1176.

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