# 53. Propellanes. LXVI. *Exo-* and *Endo-Diels-Alder* Adducts of 4-substituted 1,2,4-Triazoline-3,5-diones with Various 1,6-Methano[10]annulenes[1])

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Dedicated to Prof. Dr. *J. D. Dunitz* on the occasion of his 60th birthday

(15.X.82)

*Summary*

Relatively few *exo*-adducts have been obtained from the title compounds. Only one such mono-adduct, **3**, is known. Several *exo-endo*-bis-adducts have been obtained but the structure of one of these, **5**, has been proved unequivocally by X-ray structural determination.

We have conducted many *Diels-Alder* reactions between propellanes containing one or two cyclohexadiene rings and bridged [10]annulenes with triazolinediones [2] [3]. In such reactions one may expect *a priori* the formation of two isomeric mono-adducts, *exo* and *endo*. Although the preference for *endo*-adducts is well-known and we have obtained such mono-adducts **1** or *endo-endo*-bis-adducts **2** as shown by their X-ray, we have observed that 11-cyano-1,6-methano[10]annulene affords both isomeric *exo*- and *endo*-derivatives, **3** and **4**, and that 1,6-methano[10]-annulene itself affords the *endo-exo*-bis-adduct **5** [3a]. The correlations between the mono-adducts **3** and **4** and their *endo-endo*-bis-adduct, **2**, X = CHCN [4] have been reported [5].

A study of the crystal structures of **3** and **4** shows that **4** with or without a $C_6H_6$-molecule are sterically identical. Experiments with high-temperature diffraction methods indicate that **3** is transformed into **4** at *ca.* 175°. We explain this by simultaneous double N-inversion with a double planar transition state [5].

The bis-derivative **5** crystallizes in two forms, one of which is free of solvent whilst the other includes ethanol molecules. Both exhibit the *exo-endo*-configuration. Details of the crystal structure determinations will be published elsewhere [4] but several points of special interest ought to be mentioned.

The angles between planes L and M in **6** [6] lie in the ranges 130.8–142.4°. Opening of this angle results from the strain imposed by ring K. The values given apply for a 3-membered ring K as compared to values of 117.6–127.4° for a

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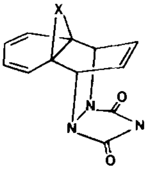
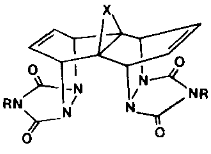
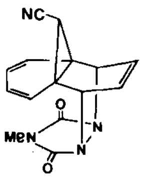
[1]) Part LXV: [1].



**1** X = $CH_2$, O, NH, NMe
R = Me, Ph



**2** X = CHY
Y = OH, OAc, Br, Me
CN, $CO_2H$, $CO_2Me$



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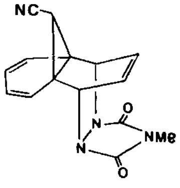
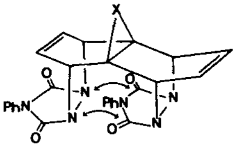
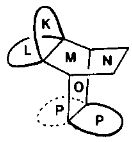


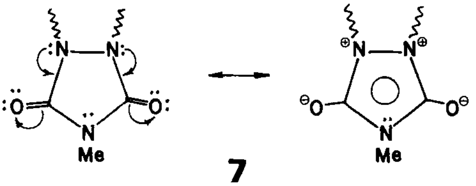
**4**



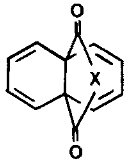
**5** X = $CH_2$, O, NH, NMe



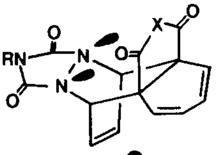
**6**



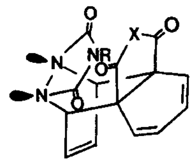
**7**



**8** X = O, NH, NR



**9**



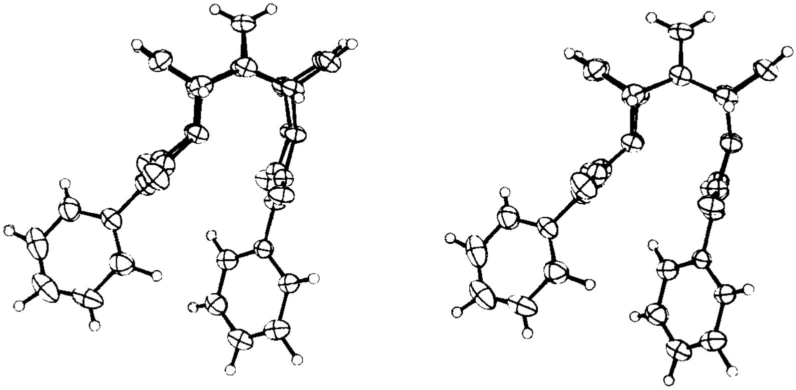
**10**

5-membered one. The triazolidinedione ring P is closer to planarity at the N-atoms in the *exo*-configuration (dotted) than in the *endo*, *i.e.* the angles between planes P and O are 150.5–157.5° in the former and 130.9–136.2° in the latter. The N-atom attached to a methyl or to a phenyl ring is usually planar in the *endo*-isomers owing to conjugation with the carbonyl groups. However, the *N*-methyl group in **3** deviates out of the plane of the triazolidinedione ring by as much as 0.398 Å, indicating the non-planarity of the N-atom to which it is attached. Perhaps this means that when the angle between planes O and P is closer to 180°, conjugation of the two vicinal N-atoms with their corresponding proximate carbonyl groups takes place, stabilizing the planar transition state **7**.

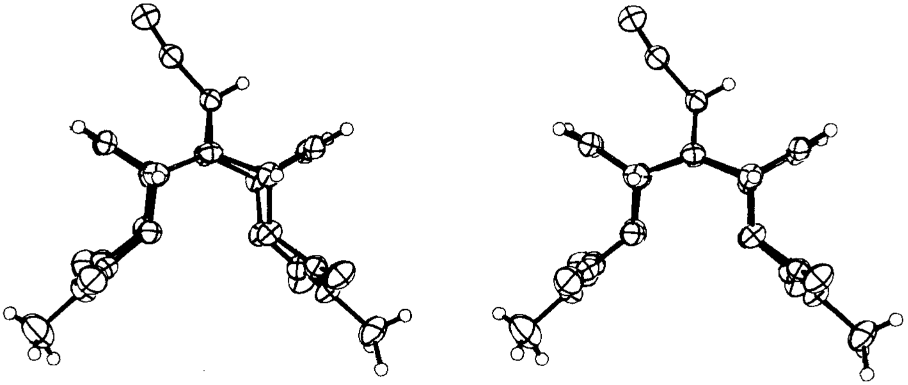
We have brought much evidence to show that in propellanes containing carbonyl groups, as in **8**, the carbonyls act as traffic policemen, ordering the dienophile to attack from the *syn*-side of the hetero-ring [7]. We have suggested that secondary orbital interactions between the CO-$\pi^*$ orbitals (LUMO) of **8** and the $n_-$-antisymmetric combination of the lone-pair orbitals in the title-dienophiles afford a more stable transition state (leading to **9**) than the obtained by *anti*-attack. It is not surprising that the *endo*-product **9** is obtained rather than its *exo*-isomer **10**, since in the latter case the lone pairs on the N-atoms would be pointing in the wrong direction, nothing being gained in stablization of the transition state.

The latter structure does not exist in *anti*-attack and there is no reason why there cannot be two transition states, one leading *e.g.* to **3** and one to **4**. Nevertheless it was only after dealing with scores of mono- and bis-*Diels-Alder* adducts that we have obtained the products of *exo*-attack **3** and **5**.

X-ray crystallography has shown [4] that the mono-*Diels-Alder* adduct of 1,6-methano[10]annulene with 4-phenyl-1,2,4-triazoline-3,5-dione has the *endo*-structure **1** ($X = CH_2$, $R = Ph$) and that the bis-adduct formed from it is **5** (see *Ortep* projection of **5**).



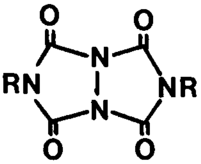
**5**



**11**

The lone pairs of the N-atoms in the *endo*-ring are optimally situated for overlap with those of the carbonyl groups in the *exo*-ring. This interaction is different from the one we have been discussing in the reactions of propellanes containing anhydride and imide rings with triazolinediones affording exclusively *syn*-attack, a secondary orbital interaction apparently being involved [7]. Calculations conducted in Heidelberg are in progress in order to ascertain whether or not this obvious idea is tenable [8]. The *Ortep* projection **11** of **2**, X = CHCN, is also given above.

We believe we have several additional bis-adducts of type **5** which like **5a** have the *anti-anti-exo-endo* structure, on the basis of their mass-spectral fragmentation leading to the fragment **12**. Unfortunately it has so far not been possible to unequivocally establish their structures by X-ray crystallography.



**12**

## REFERENCES

[1] *I. Sataty, M. Peled & D. Ginsburg,* Heterocycles *19,* 1627 (1982).

[2] a) *J. Kalo, E. Vogel & D. Ginsburg,* Tetrahedron *33,* 1177 (1977); b) *Idem,* ibid. *33,* 1183 (1977); c) *J. Kalo, J.J. Bloomfield & D. Ginsburg,* ibid., *34,* 2153 (1978); d) *J. Kalo & D. Ginsburg* ibid. *34,* 2155 (1978); e) *P. Ashkenazi, J. Kalo, A. Rüttimann & D. Ginsburg,* ibid. *34,* 2161 (1978).

[3] a) *P. Ashkenazi, E. Vogel & D. Ginsburg,* Tetrahedron *33,* 1169 (1977); b) *Idem,* ibid. *34,* 2167 (1978); c) *P. Ashkenazi, M. Peled, E. Vogel & D. Ginsburg,* ibid. *35,* 1321 (1979).

[4] *M. Kaftory,* to be published.

[5] *P. Ashkenazi, M. Kaftory, D. Arad, Y. Apeloig & D. Ginsburg,* Helv. Chim. Acta *64,* 579 (1981).

[6] *M. Kaftory,* Acta Cryst. B *36,* 597 (1980).

[7] *R. Gleiter & D. Ginsburg,* Pure and Appl. Chem. *51,* 1301 (1979) and ref. therein.

[8] *R. Gleiter,* private communication.