PROPELLANES. XCII. THE STEREOCHEMISTRY OF DIELS-ALDER REACTIONS OF TETRAENIC PROPELLANES AND OF 1,6-BRIDGED[10]ANNULENES WITH 4-SUBSTITUTED 1,2,4-TRIAZOLINE-3,5-DIONES.[1#]

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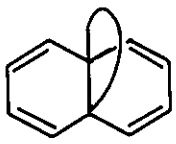
Abstract - Syn-anti, endo-exo types of configuration in the title compounds, in general, and in 11-cyano-1,6-methanol[10]annulene, as a specific case, are discussed.

INTRODUCTION

We have published much on reactions of dienophiles with various propellanes 1[2], and the title [10]annulenes, 2.[3]



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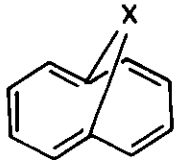


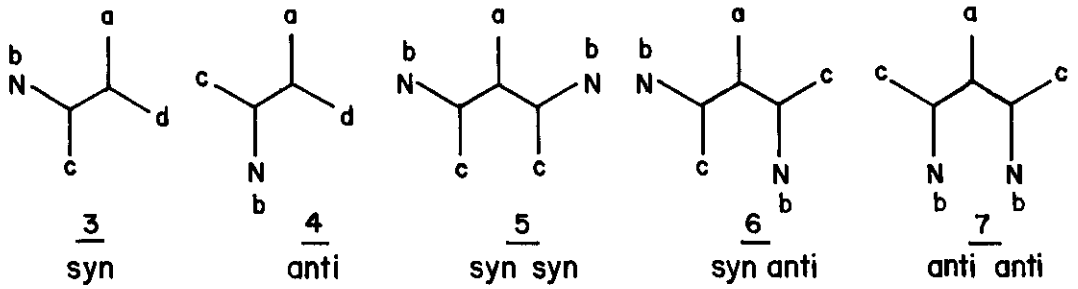
2 X=CH_2 ,O,NH, NMe

The first thrust was in the direction of syn,anti isomerism. Since 1 and 2 exhibit C_{2v} symmetry, each example is, in principle, capable of affording two isomeric mono-Diels-Alder adducts (syn and anti), and three isomeric bis adducts (syn-syn, syn-anti, and anti-anti). We soon learned that most dienophiles (including TCNE) are capable of affording only mono adducts with the title substrates[2,4] and that only the very reactive title dienophiles, i.e. with the 4-substituent either Me (MTAD) or Ph (PTAD), were capable of affording bis adducts when reacted with mono adducts with other (less reactive) dienophiles or bis adducts if reacted with the title "dienes" as substrates.

Dedicated to Professor Derek Barton on the occasion of his 70th birthday.

✡ Deceased March 9, 1988.

Thus, using our shorthand notation for the Diels-Alder products from the title components, we have 3 and 4 for the above monoadducts, 5, 6, and 7 for the corresponding bis adducts.



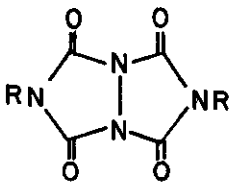
a = reference ring, e.g. cycloalkane, cyclolalkene, O,N,S, cycloalkane

b = NMe or NPh triazolidine ring

c = cyclohexene

d = cyclohexadiene

Anti, anti compounds - The above consideration of syn-anti stereoisomers has taken no account of Alder's endo-exo isomerization (too classic as to require citation). Nor did we require such accounting until we discovered that for certain bridged [10]annulenes we required the definition of endo-exo as well as syn-anti. Thus, for example we reported the formation of 8 as an important ion obtained in mass spectral fragmentation of compounds of type 7.[5] However, we did not isolate exo-endo 7 and endo-endo 7 at that time.



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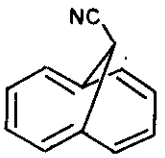
Later we isolated two different crystalline isomers of the mono MTAD adduct of 11-cyano-1,6-methano[10]annulene 9 . These adducts turned out to be 10 and 11, the anti-endo and anti-exo isomers, respectively, of type 4.[6]



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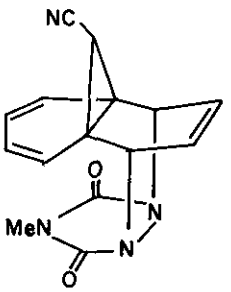

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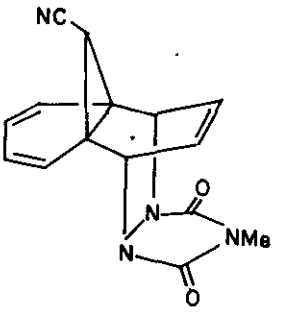


11

syn-cyano-anti-exo syn-cyano-anti-endo

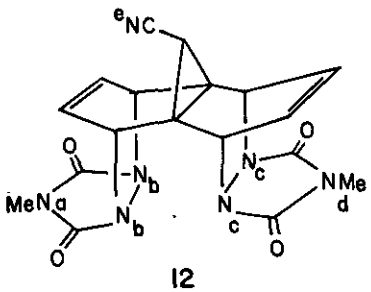
There was no question about their structures. One can view their corresponding ORTEP projections.[6] The X-ray structure of the bis adduct of 9 has also been observed.[7] It has the anti-endo-anti-endo configuration, 12. Another bis anti,anti PTAD adduct of the parent 1,6-methano[10]annulene has been isolated and studied.[8]

In the course of a general study of the nmr spectra of PTAD adducts of tetraenic propellanes[9] we have measured the ^{1}H- and ^{15}N-nmr spectra of the bis-endo adduct 12. As expected, the 400 MHz ^{1}H spectrum exhibits the typical multiplets of two different AA'XX' spin systems for the olefinic and allylic protons and two N-CH_3 singlets. The ^{15}N spectrum (40.5 MHz) shows five signals, one CN resonance (e) and two signals each for the non-equivalent tertiary nitrogens (b, c) and N-methyl groups (a, d). Whereas the cyano resonance can be assigned by virtue of its doublet structure ($^{3}J(N,H)$ = 1.0 Hz) and the typical shielding value, the other four signals are grouped in a range of only 3 ppm and are pairwise attributed to the N_b,N_c and N_a,N_d atoms on the basis of triplet ($^{2}J(N,H)$ $^{3}J(N,H)$ and quartet structures, respectively (see Table).

The significant difference in the chemical shifts of the N_b and N_c atoms and the two N-CH_3 nitrogen atoms, respectively, is remarkable, even when the effects are small. We propose a through-space orbital overlap, as indicated in 13 and supported by molecular models, to expalin the long-range influence of the cyano group. This could be checked by a comparison of the ^{15}N chemical shifts of the CN group in 12 and 14, but the latter compound has so far only been obtained in minute amounts.

δ(15N)	J(N,H)	δ	J	δ	J
a, d		c, b		e	
-247.3	<1 Hz	-249.4	2.4	-113.5	1.0
-248.1	<1 Hz	-250.2	2.4		

Chemical shifts are rel. to $CH_3{}^{15}NO_2$ as ext. reference; solvent: DMSO-d_6



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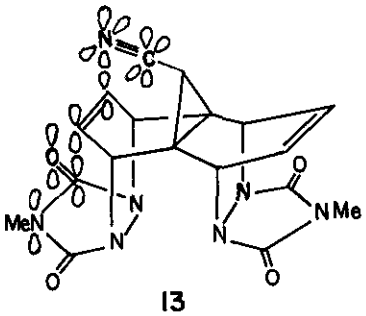

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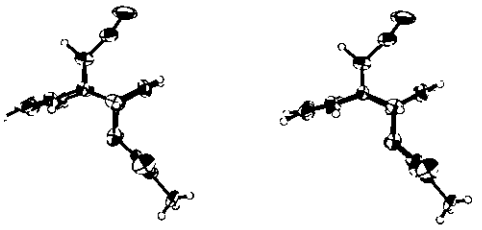
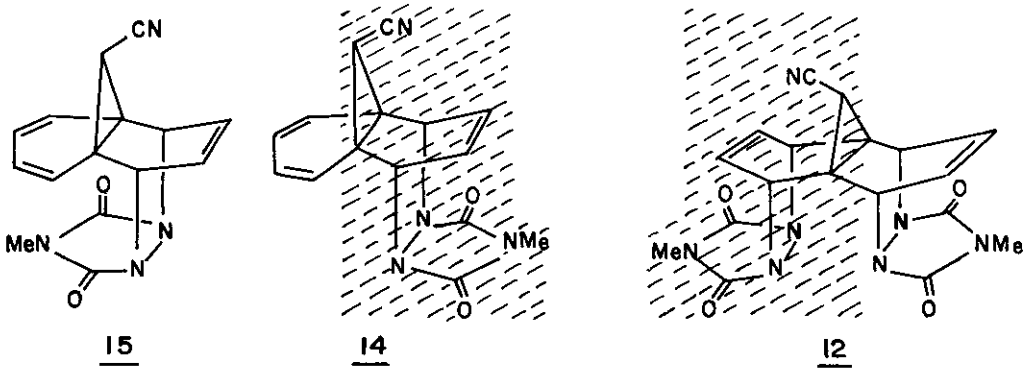
One of us (I.A.) has repeated our previous work and has been able to isolate 14 a third isomeric mono-adduct of 9, albeit in minute amount as thin yellowish transparent needles. The crystals are monoclinic ($P2_1/c$) with 8 molecules in the unit cell. X-ray structural analysis[10] proved that 14 *is the positional isomer at* C_{11}. *Like* 11 *it is anti-endo but now we must introduce a new* prefix indicating whether the CN group is syn or anti to the cyclohexadiene ring. We define 14 as the anti-cyano-anti-endo isomer; 11 is therefore the syn-cyano-anti-endo isomer, the first prefix indicating whether the CN group is anti or syn to the cyclohexadiene ring cyano-anti. Finally, the missing member of the series, is the anti-cyano-anti-exo isomer 15 which ought in any event to be thermodynamically less stable than 14. The ORTEP projection of 14 is shown.



ORTEP of 14



anti-cyano-anti-endo

CONCLUSION

Propellanes and 1,6-bridged [10]annulenes are substrates that enable us to study a variety of isomeric products which have different configurations. From our work reported herein and cited in refs. 1-7 we can generalize as follows: When the structure of the hetero-ring exhibits steric repulsion on the incoming TAD dienophile, and in [10]annulenes, anti attack occurs exclusively. When the hetero-ring is an anhydride or its imide derivatives, attack is syn to this ring due to an attractive factor.

This is in addition to the experience summarized in Alder's rule. Here too the "endo" product is more stable than its "exo" configurational isomer. In our substrates this rule holds because in general the endo isomer is the thermodynamically more stable; usually we have observed syn-endo or anti-endo products. But 11-cyano-1,6-methano[10]annulene has allowed us to isolate 3 isomers, 10, 11 and 14 out of the 4 that are possible whose structures were proved by X-ray crystallography.

It should be emphasized that these propellane derivatives of 1,6-methano[10]annulene are of the only type affording isolable anti-anti-endo or anti-anti-exo Diels-Alder adducts. Although we have results of mass spectral fragmentations of such anti, anti bis-adducts which show the bicyclic fragment 8 (see above)[5], we have not been able to show in syn,syn or in syn,anti propellanes the occurrence side-by-side of a corresponding exo- and endo-isomer on the syn side probably for reasons of repulsion between the hetero ring in the propellane adduct and the TAD moiety. In all such compounds only the endo isomer has been observed when X-ray crystallographic measurements have been carried out.[2,11]

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