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THE CRYSTAL AND MOLECULAR STRUCTURE OF PENTACYCLO[$7,8,0,0^{3,7},2^{2,8},0^{10,17}$]NONADECA-5-AZA-4,6-DIOXO-18-ENE; PROOF OF THE STEREOCHEMISTRY OF BENZENE-*CIS* CYCLOOCTENE 1,2-PHOTOADDITION.

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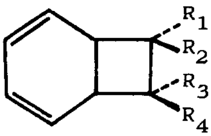

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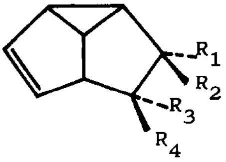

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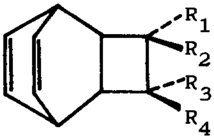

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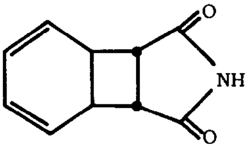
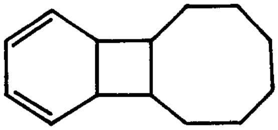


(4)

There have been many reports describing the formation of 1,2-, 1,3-, and 1,4-photoadducts of olefins with benzene ((1),(2), and (3) respectively). A number of simple olefins, on irradiation (254 nm.) in benzene solution, undergo photoaddition to the benzene ring in one or more of these modes[1,2a], and olefin stereochemistry is preserved in the concerted cycloaddition. It is considered that a preferred orientation of aromatic and addend in the ground state (dependent on the donor-acceptor nature of the two molecules) is preserved during irradiation and addition, explaining why, in every reported case, only one of the two possible isomers of (1) (*exo* or *endo*) is given[2]. The 1,2-addition of maleimide to benzene has been shown to yield *exo* (4)[3]. We now describe that the benzene-*cis* cyclooctene adduct (5) has *endo* stereochemistry.



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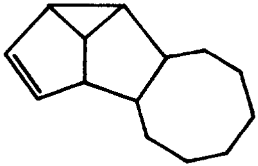

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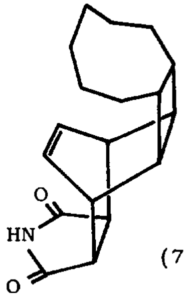


(7)

Compound (5), together with the *exo*- and *endo*-1,3-adducts (6), was obtained by irradiation of a 1:3 benzene:*cis* cyclooctene mixture using a low pressure mercury arc. Addition of maleimide to a concentrated solution of the adducts yielded white crystals of the Diels-Alder adduct (7); GLC methods showed that the 1,2-adduct had completely reacted with the dienophile and that the 1,3-adducts were completely unaffected. Elemental analysis and spectral data on the crystalline compound confirmed a 1:1:1 benzene:*cis* cyclooctene:maleimide adduct and a single crystal X-ray determination was carried out to determine the stereochemistry of the benzene-olefin fusion.

Crystal Data

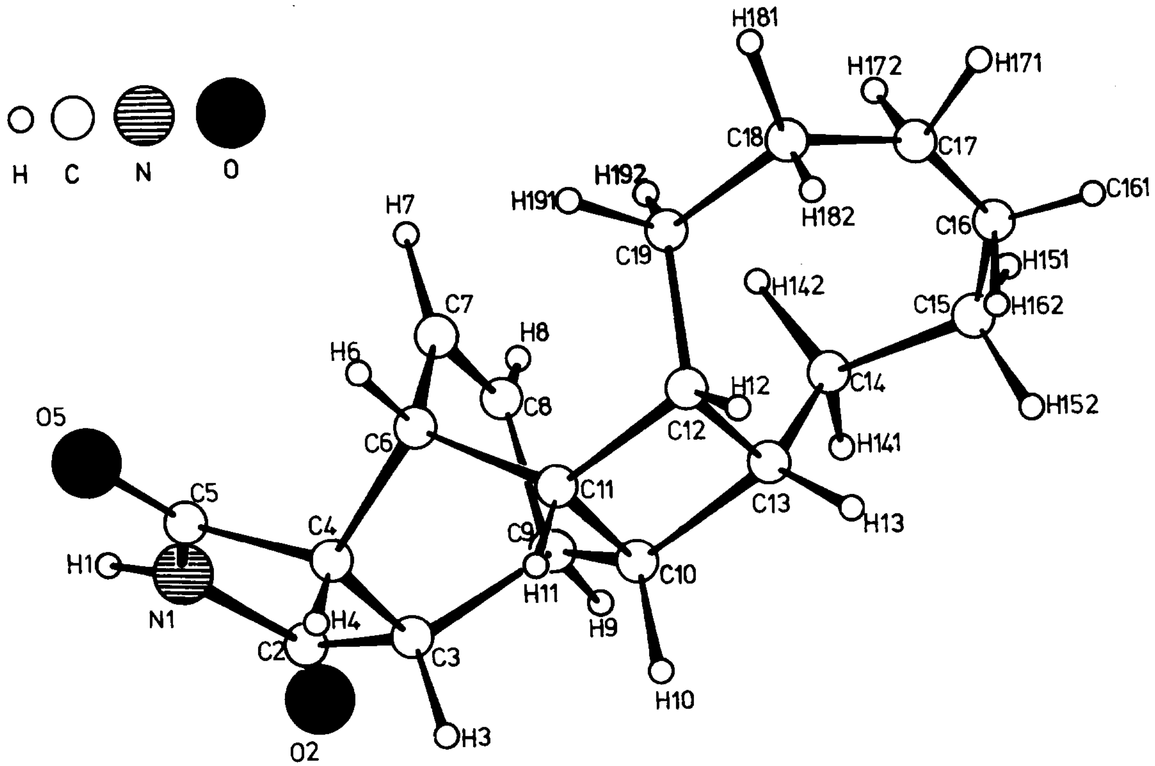
The molecule of pentacyclo$[7,8,0,0^{3,7},2^{2,8},0^{10,17}]$nonadeca-5-aza-4,6-dioxo-18-ene (formula $C_{18}H_{23}NO_2$, M.Wt. 285.4) is monoclinic, with a=13.802(12), b=6.455(8), c=17.998(12) Å, and β=113.0(1)°.

V=1545 Å^3, F(000)=616, Z=4; D_m=1.26 and D_c=1.23.

The space group is $P2_1/a$, with h01 absent for h=2n+1, and 0k0 absent for k=2n+1.

Structure Determination

The structure was solved by statistical and Fourier methods and refined by least-squares (C,N,O anisotropic, hydrogens fixed). 2015 independent reflections of 2θ<45° were measured by the stationary-crystal-stationary-counter method on a General Electric XRD5 diffractometer, of which 1293 with intensities significantly above background have been refined to R=0.116.



Discussion

The molecule of pentacyclo[7,8,0,$0^{3,7}$,$2^{2,8}$,$0^{10,17}$]nonadeca-5-aza-4,6-dioxo-18-ene is shown in the above figure together with the atomic numbering scheme. The benzene and cyclooctene residues are *endo* across the cyclobutane ring, which is planar (the dihedral angle C_{10}-C_{11}-C_{12}-C_{13}= 0.53°); in addition atoms C_9,C_{10},C_6 and C_{11} are approximately planar, as are atoms C_{13},C_{14},C_{12} and C_{19}. This arrangement makes for crowding between the unsaturated bridge and the α-CH_2's of the cyclooctane ring which is somewhat relieved by a skewing of the former (H_8-C_8-C_7-H_7= 8.5°). The cyclooctane ring is strain-free with staggered axial and equatorial protons, excepting about the C_{16}-C_{17} bond, where large thermal parameters indicate considerable vibration.

The 1,2-photoadduct, tricyclo[6,6,0,$0^{2,7}$]tetradeca-3,5-diene (5), is thus proved *endo*; to account for its formation rather than the far less crowded *exo* isomer, we have postulated *endo* association between benzene and olefin in the ground state, based on observation of the benzene-induced chemical shifts of the olefinic and α-CH_2-protons[2b].

Experimental

Photochemical apparatus: Irradiations were performed in a 250ml. fused quartz conical flask, clamped 1cm. above a flat low pressure mercury arc (7W). The photolysate was nitrogen-purged.

Method: A 3:1 olefin:benzene mixture (1200ml.) was irradiated in 150ml. aliquots, each for 75 min. (after which time, concentration of the photolabile 1,2-adduct showed no further increase). Combined photolysates were concentrated by rotary evaporation (temperature not exceeding 70°) to *ca.* 3ml. golden oil, light petrol added, and precipitated polymer filtered off. GLC analysis (C20M, 120°) showed the presence of 1,2- and 1,3-adducts. Maleimide (1g. in 10ml. diethyl ether) was added, the mixture refluxed for two hours, reduced in volume, and stood (72 hrs, 10°). A crop of white crystals (m.pt. 309-310°, subliming 250°) was recrystallised from acetone-ether to give single crystals suitable for X-ray work.

Required for $C_{18}H_{23}NO_2$: C, 75.5% H, 8.1% N, 4.9%
Found : C, 76.0% H, 8.4% N, 4.9%

Mass spectrum: M^+ 285(required for 1:1:1 adduct);175,136,110(olefin),98,78.

N.M.R. spectrum(60MHz, Trifluoroacetic acid solution): τ 3.68,tr,J=4,2H; τ 6.76,s,2H; τ 6.96,d,J=1,2H; τ 7.23,s,4H; τ 8.6,s(br),12H.

Infrared spectrum(nujol): 3260 cm^{-1}(w); 1775(m); 1710(s); 1355(m); 1195(m);690(m

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References

1.See for example: D.Bryce-Smith, A.Gilbert, B.H.Orger, Chem.Comm. 1966,512; K.E.Wilzbach and L.Kaplan, J.Amer.Chem.Soc. 1966 88 2066 and 1971 93 2073; R.Srinivasan, IBM J.Res.Develop. 1971 15 34.

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(b)D.Bryce-Smith, A.Gilbert, Hilary M.Tyrrell, Chem.Comm. 1974, 699.

3. D.Bryce-Smith, B.Vickery and G.I.Fray, J.Chem.Soc.(C) 1967, 390; D.Bryce-Smith and M.Hems, Tet.Lett. 1966, 1895.