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Crystal Structure of a Novel 1:2 Adduct from [2.2]Paracyclophane and N-Methylmaleimide

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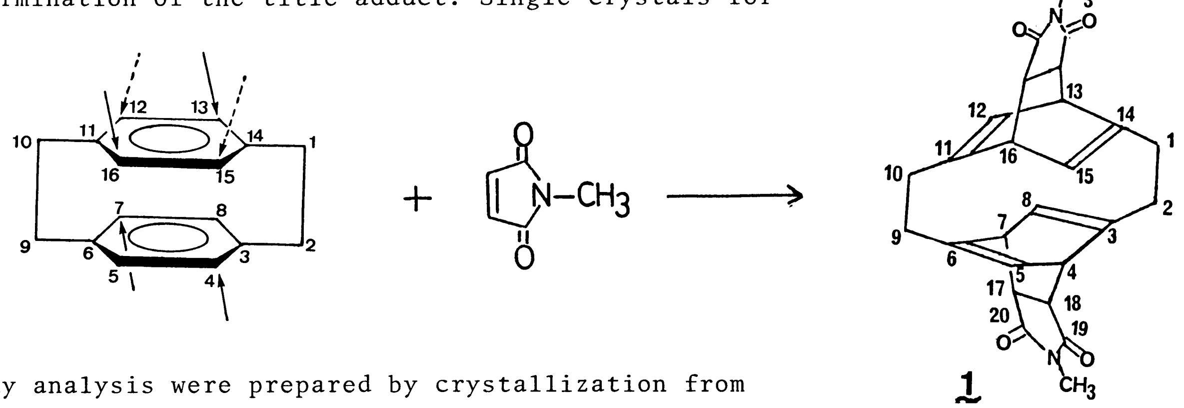
The first direct X-ray crystal structure determination of a 1:2 adduct obtained by Diels-Alder reaction of [2.2]paracyclophane and N-methylmaleimide is reported, establishing the structure arising from 4,7- and 13,16-additions.

We[1)] and others[2,3)] have described that [2.2]paracyclophane undergoes Diels-Alder reaction with either maleimides and maleic anhydride at high pressure or with "superdienophiles" such as 4-phenyl-1,2,4-triazoline-3,5-dione and dicyanoacetylene affording a novel type of 1:2 adducts. This might open up new tactics for the synthesis of chemically distinct surfaces that play an important role in surfactant chemistry and in complexation chemistry[4)] as well as in potential energy storage chemistry of strained molecules.[5)] However, the ^{13}C- and ^{1}H-NMR spectral data did not permit to determine the stereochemistry of the 1:2 adducts that can exist in two stereoisomeric forms, depending on how the two bicyclooctadi(or tri)-ene molecules are connected (i.e. depending on whether the reaction takes place in a 4,7:13,16-cross bridge or 4,7:12,15-parallel bridge fashion).

In this communication we report the X-ray structure determination of the title adduct. Single crystals for X-ray analysis were prepared by crystallization from benzene-dichloromethane.



1

Crystal data: $C_{26}O_4N_2H_{30}$, orthorhombic, space group Pbcn, a=7.815(1), b=14.620(2), c=18.717(2) Å, V=2138.5 Å^3, Z=4, D_x=1.349 g cm^{-3}, μ(Cu-K_α)=0.69 mm^{-1}.

Intensities were measured up to $2\theta=127°$ on a Rigaku AFC-5 diffractometer with Ni-filtered Cu-K_α radiation. The structure was solved by the direct method and refined by the block-diagonal least-squares method to $R=0.049(R_w=0.074)$ for 1490 reflections with $F_o<3\sigma(F_o)$. The molecular structure established by X-ray is illustrated in Figure 1, and the selected bond distances and bond angles are summarized in Tables 1 and 2, respectively. The results, therefore, have established that the reaction had occurred at 4,7- and 13,16-positions. Furthermore, each maleimide moiety occupies the same side with respect to the methylene bridge. The most intriguing and important feature in this highly strained molecule is the difference in length of the two "identical" bonds, i.e. C_1-C_2 1.539 and C_9-C_{10} 1.552 Å. Thus the two methylene bridges are irregularly twisted, in agreement with the ^{13}C-NMR chemical shifts of olefinic and methylene carbons indicating non-equivalence.$^{1)}$

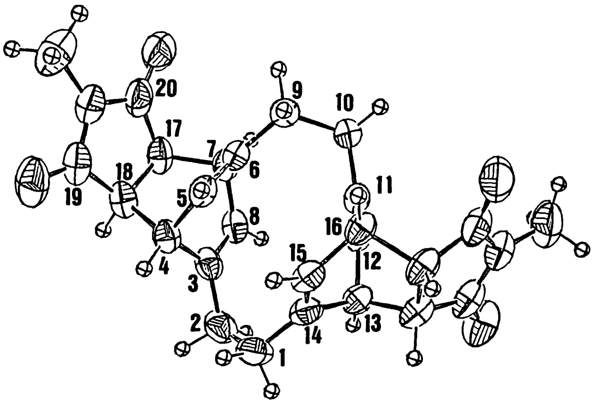


Fig. 1. ORTEP drawing of compound **1**.

Table 1. Selected bond angles

Carbon No.	Bond angle/degree (e.s.d)
5-6-7	112.7(0.18)
5-6-9	125.3(0.19)
7-6-9	121.8(0.18)
4-5-6	115.1(0.18)
3-4-5	107.8(0.17)
5-4-18	106.4(0.17)
3-4-18	104.7(0.17)
4-3-8	112.8(0.20)
2-3-4	122.1(0.20)
2-3-8	124.7(0.22)
3-8-7	115.2(0.20)
6-7-8	108.1(0.18)
6-7-17	105.8(0.18)
8-7-17	105.4(0.18)
7-17-20	111.5(0.20)
7-17-18	109.1(0.19)
18-17-20	104.8(0.20)

Table 2. Selected bond distances

Carbon No.	5-6/3-8	4-5/7-8	6-7/3-4	7-17/4-18	17-18	1-2/9-10
Bond distance/Å	1.323/1.322	1.521/1.511	1.526/1.530	1.572/1.575	1.539	1.539/1.552
(e.s.d)	(0.003)/(0.003)	(0.003)/(0.003)	(0.003)/(0.003)	(0.003)/(0.003)	(0.003)	(0.001)/(0.001)

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References

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