The Structure of the *anti* Head-to-head Photodimer of 1,1-Dimethyl-2(1*H*)-naphthalenone

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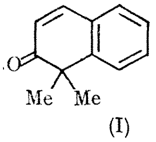
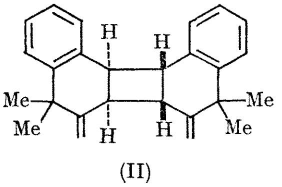
Summary Sunlight converts 1,1-dimethyl-2(1*H*)-naphthalenone completely into one photodimer shown by *X*-ray crystal analysis to be the *anti* head-to-head isomer.

THE structural and stereochemical course of the photodimerisation of enones to cyclobutanes is currently the topic of considerable research. An unsymmetrical enone can give four such dimers and, in most cases, mixtures of two or more of these are formed on photolysis.[1] Thus cyclohex-2-enone gives both *anti* head-to-head and *anti* head-to-tail isomers[2] and coumarin, in acetonitrile, gives the *syn* head-to-head and the *anti* head-to-head isomers.[3]



(I)



(II)

We find that 1,1-dimethyl-2(1*H*)-naphthalenone (I),[4] as a 0·5 M-solution in ethanol, on standing for several days in a Pyrex flask in diffuse Dundee sunlight is completely converted into a single photodimer. No other products were detectable by t.l.c. The dimer crystallised from ethyl acetate as plates, m.p. 200—204°. Its molecular weight (*m/e* 344), i.r. spectrum [ν_{max} (Nujol) 1725 cm.$^{-1}$] and n.m.r. spectrum (AA'BB' system centred at τ 6·07 and non-equivalent methyl groups at τ 8·42 and 8·64 in chloroform) showed it to be a cyclobutane dimer.

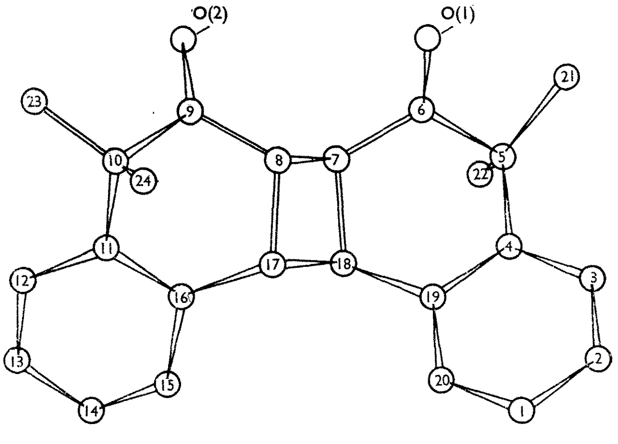


FIGURE. *Photodimer* $C_{24}H_{24}O_2$ (21, 22, 23, 24 = Me).

It was not possible, however, to decide which of the four possible configurations had been adopted an therefore determination of the structure by X-ray crystal analysis was undertaken.

The crystals were monoclinic with the following unit cell dimensions: $a = 11{\cdot}556$, $b = 12{\cdot}004$, $c = 13{\cdot}486$ Å, $\beta = 101{\cdot}0°$; space group $P2_1/n$, $Z = 4$, $D_{\text{obs}} = 1{\cdot}241$ g./cm.[3].

Three-dimensional diffraction data (3940 independent reflections) with Cu-K_α radiation were collected and the structure was determined by the direct symbolic addition procedure. The signs of 236 reflections were obtained and an "E" Fourier synthesis gave 23 peaks which were identified as atoms. A structure-factor calculation for all reflections with $E > 1{\cdot}5$ gave 110 further signs and the subsequent three-dimensional E Fourier synthesis revealed all 26 atoms. The co-ordinates from this map gave a conventional R value of 0·34 with the largest 2900 reflections and 3 cycles of least-squares refinement with isotropic temperature parameters reduced R to 0·18. Further refinement has reduced R to below 0·10 and it has been established that the structure is that of the *anti* head-to-head isomer (II). A drawing of the molecule projected on to its own mean plane is shown in the Figure. The cyclobutane ring is almost planar with deviations from the mean plane of the four atoms of less than ±0·06 Å.

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