

THE X-RAY ANALYSIS AND MOLECULAR STRUCTURE OF THE PHOTODIMER OF METHYL
NAPHTHALENE-2-CARBOXYLATE

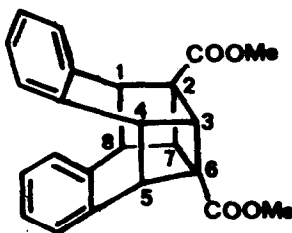
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The X-ray crystal structure analysis of the photodimer of methyl naphthalene-2-carboxylate has confirmed the cage structure (I) proposed on the basis of mass, UV and NMR spectral evidence.¹



(I)

The photodimer crystallises from ethanol as rhombs with $a = 17.015(10)$, $b = 18.112(7)$, $c = 11.921(4)$ Å; $U = 3674(5)$ Å³; $D_m = 1.333(2)$ (by flotation); $D_c = 1.347$; $\mu = 3.78$ cm⁻¹; space group Pbc_a.

Intensity data for 2697 reflexions were measured using CuK $_{\alpha}$ radiation (Ni filtered) on a Canberra Industries automated four circle Siemens diffractometer. The structure was solved by the symbolic addition procedure using 356 reflexions for which $E > 1.4$. Most atoms were revealed at that stage and progressively, all atoms including H atoms have been located. Preliminary least squares refinement of atomic positional and thermal parameters has lowered the conventional R-factor to 0.14.

Perspective views of the molecule as viewed down the a and b axes are given in Fig. 1 and 2 respectively and clearly show the cage structure formed by the photo-induced bonding of C₁, C₂, C₃ and C₄ to C₈, C₇, C₆ and C₅ respectively.

The molecule may therefore be interpreted as the product of two monomer units oriented in an eximer in such a way as to result in the maximum degree of π -overlap. This results when the monomers are parallel to and superimposed on each other.²

The dimer would possess a two-fold axis but for the mutual orientation of the ester groups and a slight twist of the aromatic rings. These are probably crystal packing distortions since the equivalent dimer of dimethyl naphthalene-1:8-dicarboxylate does possess a true two-fold axis.³

The dihedral angle formed by the aromatic rings is 66° and the tetrahedral angles at C_1 , C_8 , C_4 and C_5 are opened out to about 118° so that the minimum C...C distance between the aromatic rings is 3.0 \AA .

The ten bonds forming the three fused 4-membered rings are all significantly elongated, ranging in length from 1.56 to 1.61 \AA . This feature has been found in many cyclobutane derivatives and is accentuated here by the strain which must be present in such a cage structure. All other bond lengths lie within 2σ of their expected values.⁴

References

1. P.J. Collin, D.B. Roberts, G. Sugowdz, D. Wells and W.H.F. Sasse, Tetrahedron Letters, 1972, pp. 321.
2. J.B. Birks, "Photophysics of Aromatic Molecules" Chapter 7. Wiley-Interscience, London, 1970.
3. M. Sterns, private communication.
4. L.E. Sutton, "Tables of Interatomic Distance and Configuration in Molecules and Ions", Special Publication No. 18, Chemical Society, London, 1965.

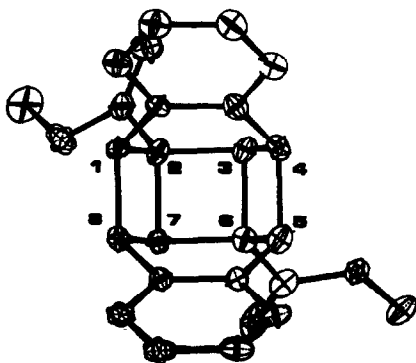


Fig. 1

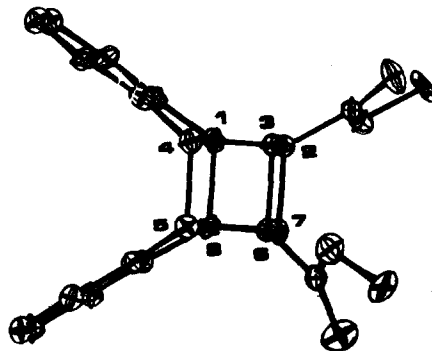


Fig. 2