The Crystal Structure of 2-Methoxynaphthalene Photodimer

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Summary Full X-ray analysis of crystals of 2-methoxynaphthalene photodimer has revealed a centrosymmetric molecular structure, different from previously suggested structures, with the two 2-methoxynaphthalene components linked in 1,4–1′,4′ positions of the substituted rings.

PHOTODIMERS of 2′-alkoxynaphthalenes were first reported by Bradshaw *et al.*[1] who suggested, on the basis of u.v. absorption spectra, that dimerization occurs in the 1,4–1′,4′ positions of the unsubstituted rings, leading to two alternative, *cis* and *trans*, structures. Since neither of these structures was compatible with the unit cell dimensions and space group obtained in our preliminary investigation of the dimers, we recently suggested a possible structure bridged in the 9,10–9′,10′ positions which appeared to be in good agreement with the observed n.m.r., u.v., and i.r. spectra.[2]

However, the full X-ray structure analysis of 2-methoxynaphthalene reported here has shown that the two halves of the dimer molecule are linked in the 1,4–1′,4′ positions of the substituted rings in a *trans*-configuration (Figure 1).

The crystals used in the analysis were prepared as described previously.[2] *Crystal data*: $C_{22}H_{20}O_2$, M = 316·4, monoclinic, a = 9·59, b = 7·89, c = 10·41 Å, β = 98·8°, U = 778 Å^3, D_m = 1·36, D_c = 1·35 g.cm.$^{-3}$, Z = 2, space group $P2_1/c$, (C^5_{2h}; No. 14), μ = 6·7 cm.$^{-1}$.

Crystals with all dimensions between 0·1 and 0·15 mm. were used to collect data around the a and b axes. Intensities of 1423 independent reflections (210 too weak to be observed) were measured using Cu-K_α radiation on an automatic computer-controlled Supper equi-inclination diffractometer and converted to structure factors without correcting for absorption. The accuracy of the data is limited to some extent by the gradual decomposition of the dimer on X-ray-irradiation.

Attempts to derive the structure from the Patterson distribution were inconclusive and the structure was solved by a reiterative sign determination process based on Sayre's equation using a modified version of R. E. Long's (UCLA, 1965) program for centrosymmetric structures. The signs of 172 reflections with normalized structure amplitudes $|E| > 1·5$ were determined and a Fourier synthesis based on these reflections revealed the positions of the oxygen and all 11 carbon atoms in the asymmetric unit. The 10 hydrogen atoms were located from difference syntheses. The structure was refined by full-matrix least-squares calculations. In the final cycles the carbon and oxygen atoms were given anisotropic temperature parameters, the

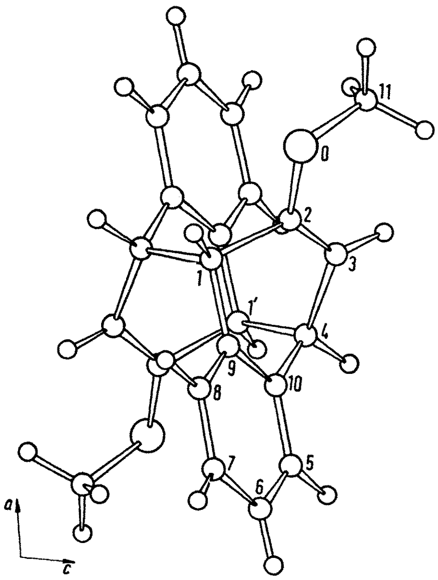

FIGURE 1. *One dimer molecule viewed down the* b-*axis.*

isotropic hydrogen temperature parameters being held constant. At present R is 0·06 for the observed reflections.

The bond lengths and angles are shown in Figure 2. Average standard deviations are 0·005 Å for C–C and C–O, 0·05 Å for C–H bonds, 0·3° for "heavy atom" angles, 2° for C–C–H angles, and 2·5° for angles involving methyl hydrogens. The dimer molecules are centrosymmetric, with centres of molecules lying on centres of crystallographic symmetry. The length of the bridging bond C(1)–C(4′)—1·61 A—agrees with the corresponding bond distances observed in the photodimers of anthracene[3] and 9-anthraldehyde,[4] to which the present structure is very similar. The aromatic rings are planar within experimental error. In the nonaromatic rings the angle between the two "boat" planes C(1), C(9), C(10), C(4) and C(4), (C3), C(2), C(1) is 132°, comparable to 134° in the anthracene dimers.[3,4]

The decomposition of the dimer crystals on irradiation with X-rays, observed on exploratory Weissenberg photographs taken after increasing periods of irradiation, shows some peculiar features. The initially single phase pattern of the dimer, after approximately 75 hr. exposure to Cu-K_α radiation, begins to show a superimposed single crystal pattern of monomeric 2-methynaphthalene (together with a second as yet unidentified phase), which increases in intensity on further irradiation, attaining almost equal intensity with the dimer pattern after about 200 hr. After 300 hr., the pattern of the decomposition products begins to fade and disappears almost completely after about 500 hr., leaving the initial dimer pattern with diminished intensity. The irradiated crystals, although retaining the initial shape, have turned opaque at this stage. It thus appears that on X-ray-irradiation the dimer reverts partially to the monomer in an ordered state which on further irradiation is gradually expelled from the crystal.

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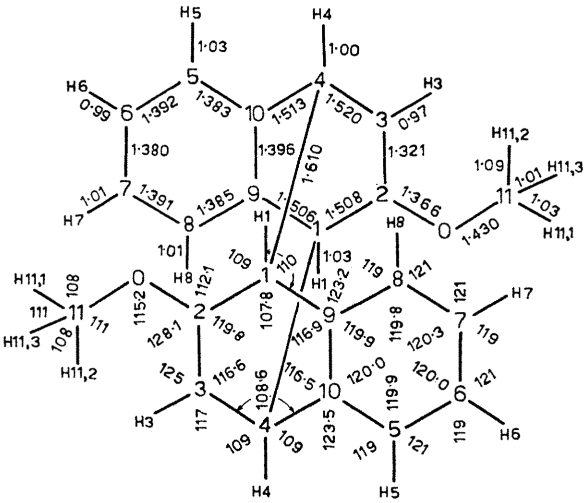

FIGURE 2. *Bond distances* (Å) *and angles. Angle* C(2)–C(1)–C(4′) = 110·6° C(4′)–C(1)–C(9) = 111·6°, C(4′)–C(1)–H(1) = 108°, C(3)–C(4)–C(1′) = 111·6°, C(1′)–C(4)–C(10) = 111·2°, C(1′)–C(4)–H(4) = 107°, O–C(11)–H(11,3) = 108°, H(11,1)–C(11)–H(11,2) = 111°.

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