

DIMERIC 2-ALKOXYNAPHTHALENES*

By META STERNS† and B. K. SELINGER†

The irradiation of 2-methoxynaphthalene in solution gives a dimer whose insolubility and lability renders further chemical investigation difficult.¹ The dimeric nature of the product was confirmed by the mass spectrum which showed a base peak at m/e 316 due to the molecular ion.² The kinetics and thermodynamics of the formation of an excimer by both 1- and 2-methoxynaphthalene had shown that the latter was considerably more stable. Although the kinetics of formation of photodimer parallel that of formation of excimer there was no evidence that the excimer is a kinetic intermediate.²

The photodimers of a series of 2-n-alkyloxynaphthalenes (i.e., methyl, ethyl, propyl, and n-pentyl) were prepared by irradiating the monomer in its lowest (L_b) singlet band with either the Hg 313-m μ line or sunlight through Pyrex. The branched isopropylloxynaphthalene does not appear to form a photodimer. When prepared by irradiation of the melt the dimer crystals were perfectly clear.

X-ray measurements on single crystals yielded the following data:

2-Methoxynaphthalene.—Monoclinic; $a = 9.59 \pm 0.02$, $b = 7.98 \pm 0.01$, $c = 10.41 \pm 0.02$ Å; $\beta = 98.8^\circ$; $V = 787.3$ Å³; $Z = 2$; $D_m = 1.36$ g cm⁻³; $D_x = 1.33$ g cm⁻³.

2-Propylloxynaphthalene.—Monoclinic; $a = 12.5$, $b = 8.0$, $c = 10.4$ Å; $\beta = 105^\circ$; $V = 1001$ Å³; $Z = 2$; $D_m = 1.22$ g cm⁻³; $D_x = 1.23$ g cm⁻³.

Systematic absences.— $0k0$ for odd k , $h0l$ for odd l .

The cell dimensions for the methyl dimer were obtained using powdered silicon as an internal standard. The maximum deviation from the mean is the error quoted. The structure was thus assigned to space group $P2_1/c$ (No. 14). The clear photodimer crystals became opaque on prolonged X-irradiation. Ghost spots also appear which are probably due to the formation of monomer retaining the dimer configuration and on further irradiation these disappear with the simultaneous appearance of monomer powder streaks.

The cell dimensions a of the other n-alkyl derivatives were determined (by D. Wilson in this Laboratory) from powder diffraction patterns: methyl, 9.6; ethyl, 11.0; n-propyl, 12.5; n-pentyl, 14.3.

Since the $0kl$ reflections appear at the same angle in all the compounds, the b and c dimensions are virtually independent of the alkyl substituents, indicating that these lie along the a -axis. This in turn sets an upper limit for the length of a dimer molecule which rules out the *trans* 1,4-1',4' structure previously suggested. The *cis*

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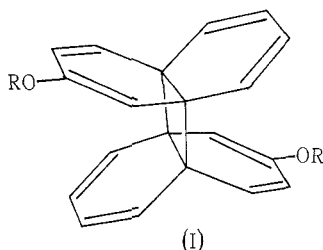
† Department of Chemistry, School of General Studies, Australian National University, Canberra, A.C.T. 2600.

¹ Bradshaw, J. S., and Hammond, G. S., *J. Am. chem. Soc.*, 1963, **85**, 3953.

² Wiliarat, Prapin, and Selinger, B., *Aust. J. Chem.*, 1968, **21**, 733.

1,4-1',4' addition product will not be centrosymmetric as required by the crystal space group.*

The assumption that a pseudo-centre of symmetry is most unlikely leads one to consider the structure (I) for the dimers ($R = \text{Me, Et, Pr}^n, n\text{-C}_5\text{H}_{11}$).

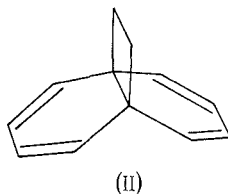


The spectroscopic evidence provides strong support for such structures.

Dissolution of (I; $R = \text{Me, Et, Pr}^n, n\text{-C}_5\text{H}_{11}$) in deuterochloroform to determine the n.m.r. spectrum (60 Mc/s) was always accompanied by some decomposition, with the production of the corresponding monomeric alkoxy-naphthalene. Hence the spectrum of (I; $R = \text{Me}$) showed methoxy singlets at τ 6.15, 6.25, the former corresponding to 2-methoxynaphthalene; aromatic protons from the monomer; and dimer olefinic protons. In no dimer could any methine (bridgehead) absorption be detected. Bridge-bonding in the 9 and 10 positions is the only possibility which does not necessitate the presence of such protons. Acid catalysis rapidly converted all the dimer into the corresponding monomer.

Deuteration studies showed that the highest-field olefinic absorption (2H, singlet, τ 4.3) of (I; $R = \text{Me}$) is in fact due to the 1- and 1'-protons. The remaining olefinic protons show absorption in the region τ 2.9-4.0.

The lack of aromaticity in the dimers (I) is also supported by the i.r. spectra. The spectra (Nujol) showed strong absorption at 1650, 1280, 1210, 1150, 1010, 770, and 785 cm^{-1} but no absorption characteristic of aryl alkyl ethers (1250 cm^{-1}), aromatic C-H, C-C bonds (1515 and 1600 cm^{-1}), or the aromatic substitution pattern (900, 875, 845, 817 cm^{-1}). All these bands are prominent in the i.r. spectra of the monomeric alkoxy-naphthalenes.



Furthermore, the ultraviolet spectra are not unlike that observed for 9,10-ethano-9,10-dihydronaphthalene³ (II): λ_{max} 235, 284 $\text{m}\mu$ (ϵ 4700, 2200). The ultraviolet

* Note added in proof.—This would seem to rule out the structures recently suggested by Bradshaw, J. S., *et al.*, *J. org. Chem.*, 1968, **33**, 259.

³ Vogel, E., Maier W., and Eimer, J., *Tetrahedron Lett.*, 1966, 655.

spectrum (methylene chloride) of (I; R = Me, Prⁿ) showed maxima at 273, 283 m μ (ϵ 2900, 3500). An absorption maximum at shorter wavelength (*c.* 232 m μ) occurs but is difficult to measure accurately.

It has been shown² that the formations of excimers and photodimers follow similar kinetics although there was no evidence to suggest a consecutive reaction. The assumption of an excimer intermediate is interesting in view of the fact that in naphthalene the "butterfly" or else the "twist" vibration drops from *c.* 180 to *c.* 135 cm⁻¹ in the excited state.⁴ In an excimer of naphthalene this weakening may be shared by both molecules and thus bonding across the 9,10-9',10' in the alkoxy-naphthalenes may become quite favourable.

The suggested structure seems more in keeping with the lability of the compound than a structure analogous to the dianthracenes.

⁴ Ross, I. G., personal communication.