concentration.[10] In accord with these observations, we have noted large proton shifts for this compound that are concentration dependent.

Finally, we have observed large changes in the n.m.r. spectra of several nickel chelates of salicylaldimines on the addition of pyridine together with corresponding shifts in the proton resonances of pyridine. Such effects are consistent with a coordination of pyridine to nickel and studies are being continued.

The chelates prepared for this study were obtained either by treating the Schiff base phenolate ion with nickel acetate or, more conveniently, by treating a suspension of the bis-(salicylaldehyde)-nickel(II) in boiling ethanol with an excess of the substituted aniline.[11,12] The chelates were obtained as anhydrous solids and had satisfactory C, H, N and Ni analyses.

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[12] L. Sacconi, P. Paoletti and G. Del Re, *ibid.*, **79**, 4062 (1957).

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THE PHOTODIMERIZATION OF MONOMETHYL FUMARATE

Sir:

Through the courtesy of Dr. G. W. Griffin we have had access to his work (since published[1,2]) on the photodimerization in the solid state of fumaric acid derivatives to the corresponding cyclobutanes. Following our own interest in the photodimerization of cinnamic acids to α-truxillic and β-truxinic acids and the dependence of the stereochemical course of this reaction on the lattice geometry of the monomer,[3] we have extended Griffin's work on the fumaric derivatives by crystallographic studies. As Griffin, *et al.*, have already noted the packing arrangements of dimethyl fumarate[4] and of fumaronitrile[5] (see Table I) favor the formation of dimers of symmetry 2/m through the contact of parallel molecules along the shortest translation period of 4 Å.

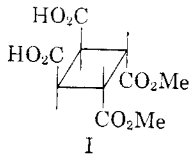
TABLE I

trans-Compound	*a*, Å.	*b*, Å.	*c*, Å.	α	β	γ	Space group	*n*
$MeO_2CCH{=}CHCO_2Me$[4]	3.92	9.24	5.93	101° 47′	112° 49′	109° 20′	$P\bar{1}$	1
$NCCH{=}CHCN$[5]	3.89	5.60	11.54	...	121.9°	...	$P2_1/n$	2
$MeO_2CCH{=}CHCO_2H$	14.14	3.99	5.60	72.6°	98.8°	83.8°	$P\bar{1}$	2
β-$PhCH{=}CHCO_2H$	6.05	4.04	31.3	...	90.3°	...	$P2_1/c$	4
$MeO_2C(CH{=}CH)_2CO_2Me$	7.74	5.81	5.82	88.0°	121.8°	106.1°	$P\bar{1}$	1
$MeO_2C(CH{=}CH)_3CO_2Me$	7.60	5.99	13.06	81.4°	107.7°	105.9°	$P\bar{1}$	2

A crystallographic survey of other fumaric acid derivatives shows that monomethyl fumarate crystallizes in a packing arrangement similar to that of the diester. It was therefore of interest to test its photo-behavior, which had not been reported by Griffin. Ultraviolet irradiation of a powdered sample of monomethyl fumarate produced a progressive change in the X-ray powder pattern. After several days of exposure the irradiated sample was washed free from starting material with diethyl ether; the less soluble residue showed no hydrogen uptake on attempted catalytic hydrogenation. After recrystallization from di-*n*-butyl ether this material melted at 153–154°; elemental analysis gave: C, 46.5; H, 4.4; (O) CH_3, 11.5. Calcd. for $C_{10}H_{12}O_8$: C, 46.2; H, 4.7; (O) CH_3, 11.6.

A convenient method of isolation of the dimeric material treats the irradiated sample with excess boiling thionyl chloride which removes the monomer at the water pump as the volatile β-(chloroformyl) methylacrylate. The anhydride of the dimer (m.p. 144° from chloroform) gives an infrared spectrum characteristic of a five-membered cyclic anhydride. Hydrolysis with hot water regenerates the diacid diester of m.p. 153–154°.

The photodimer as well as its anhydride were converted by methanolic hydrogen chloride to a compound identical with cyclobutane 1,2,3,4-tetracarboxylic acid tetramethyl ester of m.p. 144–145° obtained by Griffin and co-workers by the photodimerization of dimethyl fumarate.[2] The conformation of the dimer of monomethyl fumarate is therefore established as I. Thus, the crystal structures of the three monomers have in common a shortest axis of 4 Å. and dimerization to dimers of symmetry *m;* they are completely analogous to the β-modification of substituted cinnamic acids defined by shortest axes of 4.0 ± 0.1 Å. and photodimerization to β-truxinic acids.



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The next higher homologs, dimethyl *trans,trans*-muconate and dimethyl *all-trans*-hexatriene dicarboxylate, do not belong to this structure type (*see* Table I); work on their photochemical behavior is under way.

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