at room temperature 15–20 h and worked up with saturated ammonium chloride and ether. The product was chromatographed on silica with 2:3 diethyl ether/light petroleum ether: 74%; 200-MHz ^{1}H NMR (CDCl$_3$) δ 0.78 (s, 3, CH_3), 1.21 (d, 1, pinyl CH), 1.24 (s, 3, CH_3), 1.29 (s, 3, CH_3), 2.03–2.39 (m, 5, pinyl CH), 3.79 (s, 3, OCH_3), 3.86 (s, 3, OCH_3), 3.67–3.97 (m, 4, CHOC), 4.27 (dd, 1, CHOB), 4.48–4.81 (m, 8, CH_2O), 6.7–6.9 (m, 3, C$_6$H$_3$), 7.2–7.3 (m, 15, C$_6$H$_5$). Anal. Calcd for $C_{44}H_{53}BO_8$: C, 73.33; H, 7.41; B, 1.50. Found: C, 73.30; H, 7.75; B, 1.45.

(*s*)-Pinanediol (1*R*,2*R*,3*S*)-[1-Hydroxy-2,3,4-tris(benzyloxy)butyl]boronate (3b). Treatment of **2b** with DDQ under the conditions used for the preparation of **3a** from **2a** yielded 86% **3b** as an oil: 200-MHz ^{1}H NMR (CDCl$_3$) δ 0.7 (s, 3, CH_3), 1.19 (d, 1, pinyl CH), 1.23 (s, 3), 1.24 (s, 3) (CH_3's), 1.8–2.2 (m, 5, pinyl CH), 3.6–3.9 (m, 5, CHO), 4.02 (d, br, 1, OH), 4.25 (dd, 1, CHOB), 4.4–4.7 (m, 6, PhCH_2O), 7.2–7.4 (m, 15, C$_6$H$_5$). Anal. Calcd for $C_{35}H_{43}BO_6$: C, 73.68; H, 7.60; B, 1.89. Found: C, 73.46; H, 7.83; B, 1.84.

(*s*)-Pinanediol (1*R*,2*R*,3*S*)-[1-[(Methylsulfonyl)oxy]-2,3,4-tris(benzyloxy)butyl]boronate (4b). Treatment of **3b** methanesulfonyl chloride under the conditions used for conversion of **3a** to **4a** yielded 90% of crude **4b**: 90-MHz ^{1}H NMR (CDCl$_3$) δ 0.78 (s, 3, CH_3), 1.20 (d, 1, pinyl CH), 1.25 (s, 3), 1.26 (s, 3) (CH_3's), 1.5–2.15 (m, 5, pinyl CH), 2.90 (s, 3, CH_3SO$_2$), 3.6–3.7 (m, 3), 4.03 (dd, 1, CHOB), 4.29–4.56 (m, 4), 4.70 (s, 2), 4.76 (d, 1), 5.06 (d, 1), 7.2–7.4 (m, 15, C$_6$H$_5$). This unstable compound was used directly in the next step.

(*s*)-Pinanediol (1*S*,2*R*,3*S*)-[1,2,3,4-Tetrakis(benzyloxy)butyl]boronate (5b). Reaction of **4b** to lithium benzyl oxide in THF under the conditions described for the conversion of **4a** to **5a** followed by flash chromatography yielded 70% **5b**: 200-MHz ^{1}H NMR (CDCl$_3$) δ 0.79 (s, 3, CH_3), 1.17 (d, 1, pinyl CH), 1.25 (s, 3), 1.27 (s, 3) (CH_3's), 1.8–2.5 (m, 5, pinyl CH), 3.7–4.1 (m, 5, CHOC), 4.26 (dd, 1, CHOB), 4.5–4.8 (m, 8 PhCH_2O), 7.2–7.4 (m, 20, C$_6$H$_5$). Anal. Calcd for $C_{42}H_{49}BO_9$: C, 76.36; H, 7.48; B, 1.64. Found: C, 76.31; H, 7.91; B, 1.61.

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Registry No. **1a**, 89618-77-9; **1b**, 110488-65-8; **2a**, 110488-62-5; **2b**, 110488-66-9; **2c**, 109737-32-8; **3a**, 110488-63-6; **3b**, 110488-67-0; **4a**, 110488-64-7; **4b**, 110488-68-1; **5a**, 110548-88-4; **5b**, 110488-69-2; lithium *p*-methoxybenzyl oxide, 57965-13-6.

Solid-State Photoreactivity of Ethyl (*E*)-α-Cyano-2-methoxycinnamate

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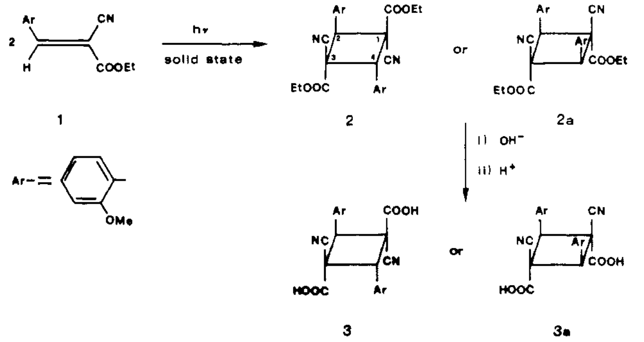
The reinvestigation of the solid-state photoreactivity of ethyl (*E*)-α-cyano-2-methoxycinnamate (1) allowed us to obtain the corresponding dimer which was shown to be diethyl (1α,2α,3β,4β)-1,3-dicyano-2,4-bis(2-methoxyphenyl)cyclobutane-1,3-dicarboxylate (2) whose structure was proven on the basis of chemical reactivity and spectroscopic data.

A large number of studies on the solid-state photoreactivity of cinnamic acids[1] and styryl derivative compounds[2] showed that the cyclobutane dimers formed had the configuration expected on the basis of the topochemical postulate.[1] In particular, (*E*)-α-cinnamic acid and (*E*)-β-4-chlorocinnamic acid gave α-truxillic acid and 4,4′-dichloro-β-truxinic acid, respectively.

During the study of the solid-state photoreactivity of 3-methyl-4-nitro-5-styrylisoxazoles,[3] we were attracted by the findings of Baker and Howes[4] who reported that the solid-state irradiation of the yellow ethyl (*E*)-α-cyano-2-methoxycinnamate (1) gave a colorless compound with a molecular weight in agreement with a dimer $C_{26}H_{26}N_2O_6$, which was described as "probably one stereoisomer of diethyl 1,3-dicyano-2,4-bis-*o*-methoxyphenylcyclobutane-1,3-dicarboxylate" (truxillic acid structure). Truxinic type structures were not considered for the above dimer.

Following our interest in the preparation of α-truxillic acids via 3-methyl-4-nitro-5-styrylisoxazole photodimers,[3] we decided to reinvestigate the photobehavior of the title compound in order to attribute a configuration of the photodimer and to search for a new entry for the synthesis of diarylcyclobutanedicarboxylic acids.

Scheme I



Results and Discussion

Solid compound 1, prepared according to the literature,[4] was irradiated with sunlight[4] or with a mercury lamp. In both cases, the colorless dimer was obtained in agreement with the previous findings. This solid was recognized as the dimer of 1 on the basis of the melting point[4] and mass spectra, which showed peaks at m/e 462 and 231 attributable to M$^+$ of the dimer and to the symmetric fragment ArCH=C(CN)CO$_2$Et]$^+$, respectively. The absence of the fragment ArCH=CHAr]$^+$ together with the above findings is in agreement with a truxillic type structure for the

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0022-3263/87/1952-5124$01.50/0

Table I. ^{1}H and ^{13}C NMR Data (DMSO-d_6) for Compounds 2–5 and 7[a]

compd	^{1}H NMR	^{13}C NMR
2[b]	0.94 (t, 6 H, 2 × OCH_2CH_3), 3.87 (s, 6 H, 2 × OCH_3), 4.04 (q, 4 H, 2 × OCH_2), 5.31 (s, 2 H, cyclobutane), 6.85–7.60 (m, 8 H, 2 × Ar H_4)	13.3 (q, OCH_2CH_3), 47.7 (d, C2), 47.9 (s, C1), 54.6 (q, OCH_3), 62.8 (t, OCH_2), 110.2 (d, C3′), 117.3 (s, CN), 120.5 (d, C5′), 121.35 (s, C1′), 128.9 (d, C4′/C6′), 129.9 (d, C6′/C4′), 157.1 (s, C2′), 166.0 (s, CO)
3	3.78 (s, 6 H, 2 × OCH_3), 5.14 (s, 2 H, cyclobutane), 6.55 (br s exch, 2 × CO_2H), 6.90–7.60 (m, 8 H, 2 × Ar H_4)	47.1 (d, C2), 47.7 (s, C1), 54.9 (q, OCH_3), 111.05 (d, C3′), 118.2 (s, CN), 120.3 (d, C5′), 122.0 (s, C1′), 128.9 (d, C4′/C6′), 129.8 (d, C6′/C4′), 157.1 (s, C2′), 167.4 (s, CO)
4	3.82 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 3.95–4.85 (m, 4 H, cyclobutane), 6.85–7.75 (m, 8 H, 2 × Ar H_4)	30.2 (d, C1 and C3), 36.1 (d, C4/C2), 42.1 (d, C2/C4), 55.1 (q, OCH_3), 55.3 (q, OCH_3), 111.0 (d), 111.5 (d), 119.0 (s, CN), 120.3 (d), 120.45 (d), 123.4 (s), 126.2 (s), 126.7 (d), 129.15 (d), 129.5 (d), 129.6 (d), 157.0 (s), 157.5 (s)
5	3.86 (s, 6 H, 2 × OCH_3), 4.20–4.70 (m, 4 H, cyclobutane), 6.95–7.60 (m, 8 H, 2 × Ar H_4)	30.2 (d, C1 and C3), 38.5 (d, C2 and C4), 55.45 (q, OCH_3), 111.1 (d, C3′), 119.25 (s, CN), 120.4 (d, C5′), 124.1 (s, C1′), 127.3 (d, C4′/C6′), 129.5 (d, C6′/C4′), 157.0 (s, C2′)
7	3.86 (s, 6 H, 2 × OCH_3), 4.20–4.65 (m, 4 H, cyclobutane), 6.80–7.50 (m, 8 H, 2 × Ar H_4), 11.8 (v br s exch, 2 × CO_2H)	36.1 (d, C1/C3), 44.7 (d, C2/C4), 55.4 (q, OCH_3), 110.6 (d, C3′), 120.1 (d, C5′), 127.1 (d, C4′/C6′), 127.6 (d, C6′/C4′), 127.8 (s, C1′), 157.2 (s, C2′), 173.4 (s, CO)

[a] Multiplicities determined by APT technique[6] and/or from coupled spectra. [b] Spectra recorded in $CDCl_3$.

photodimer, thus excluding the truxinic ones.

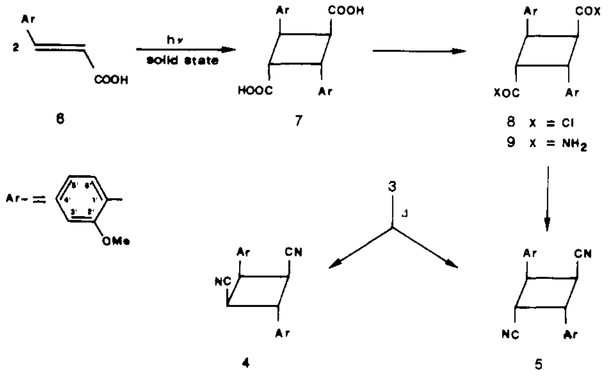
From inspection of the truxillic stereoisomers for $C_{26}H_{26}N_2O_6$ and considering the *E* configuration of **1**, it is possible to accept only the α- and ϵ-truxillic type structures **2** or **2a** for the dimer (Scheme I), that is, those deriving from *E*–*E* photocycloaddition of compound **1**.

This hypothesis is confirmed from the ^{1}H NMR spectrum of the dimer (Table I), which showed only one signal at δ 3.87 for the two methoxy groups together with the expected pattern for two equivalent ethoxy groups. In addition, the ^{13}C NMR spectrum showed only 13 lines in agreement with **2** or **2a**. At this stage, in order to attribute a configuration to the photodimer, it is necessary to discover whether the methoxyphenyl groups are 1,3-trans as in **2** or 1,3-cis as in **2a**. To solve this problem, information was obtained by alkaline hydrolysis of the dimer, which gave, after acidification, the corresponding dicarboxylic acid **3** or **3a**. The ^{1}H NMR spectrum of the above acid showed again only one signal for the two *o*-methoxy groups and 11 lines in the ^{13}C NMR spectrum. These results confirm that the acid has the same configuration as the corresponding ester dimer and therefore that no isomerization occurred during the hydrolytic process.

In order to attribute a configuration to the acid and to the dimer, we decided to decarboxylate the acid to the corresponding dinitrile and to search for an alternative synthesis for this compound.

As expected, compound **3** or **3a** could be easily decarboxylated by heating near its melting point. However, HPLC, TLC, and ^{1}H NMR analysis of the crude reaction mixture showed that from the solid thermal reaction two cyclobutanedinitriles (mp 144–145 °C and mp 178–179 °C) were formed together with minor amounts of secondary products instead of the expected single product. Among the secondary products, it was possible to recognize (^{1}H NMR) the presence of (*E*)- and (*Z*)-2-methoxycinnamonitriles deriving from cylobutane ring rupture during thermal decarboxylation. When the thermolysis was carried out in solution, only the two dinitriles were obtained. Mass spectra of these compounds gave the same M^+ (*m*/*e* 318) and showed a superimposable fragmentation pattern. These features, besides confirming that the two samples are isomers, gave no additional information and seemed to complicate the correlation of the configuration of the dinitriles with that of the acid. However, assuming that the dimer had the structure **2**, the dinitriles should be **4** and **5**; accordingly, we prepared the 2,2′-dimethoxy-α-truxillodinitrile **5** by the usual procedure starting from the corresponding 2,2′-dimethoxy-α-truxillic acid, which in turn was synthesized by photodimerization of solid (*E*)-2-methoxycinnamic acid (**6**). The dinitrile obtained by this route is identical (melting point, HPLC, TLC, IR, ^{1}H NMR, and ^{13}C NMR) with the previous sample with mp 178–179 °C.

Scheme II



These results confirm that the methoxyphenyl groups in compound **5** are 1,3-trans and therefore have the same configuration in the acid and in the dimer, which therefore have the structures **3** and **2**, respectively; structures **2a** and **3a** are ruled out. The two dinitriles **4** and **5** obtained by thermolysis should differ only in the configuration of the cyano groups, which are trans in **5** and therefore must be cis in isomer **4**. This assumption was confirmed from the ^{1}H and ^{13}C NMR spectra of **4** and **5** (Table I); in fact, the two methoxy groups of **5** showed only one peak at δ 3.86, whereas those of **4** appear separated (δ 3.85 and δ 3.82). In addition, the ^{13}C NMR spectrum of compound **5** showed only 10 lines, whereas compound **4** gave rise to 18 lines, strongly indicating different symmetry between **4** and **5**.

It is thus confirmed experimentally that **4** differs from **5** only in the configuration of the cyano groups; therefore, while **5** is 2,2′-dimethoxy-α-truxillodinitrile, compound **4** is 2,2′-dimethoxy-γ-truxillodinitrile.

In conclusion, the photodimer $C_{26}H_{26}N_2O_6$ is diethyl ($1\alpha,2\alpha,3\beta,4\beta$)-1,3-dicyano-2,4-bis(2-methoxyphenyl)cyclobutane-1,3-dicarboxylate (**2**) and the corresponding acid has the structure **3**; in addition, finding the two dinitriles **4** and **5** instead of the expected **5** alone could be rationalized through the decarboxylation mechanism, which may involve the formation of carbanions at C-1 and/or C-3 of the cyclobutane ring, which then may or may not invert configuration as a result of C–H bond formation.

Experimental Section

Melting points were taken on a Büchi 510 apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Perkin-Elmer R32 90-MHz instrument and ^{13}C NMR spectra were obtained by the Fourier transform technique with a Varian FT-80A (20-MHz

^{13}C) spectrometer; chemical shifts are reported in ppm downfield from internal tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer 283 spectrophotometer. Mass spectra were taken on a VG 70-70 EQ spectrometer. Thin-layer chromatography (TLC) was carried out with silica gel 60 plates (Merck F_{254}). Chromatographic separations were performed by using Merck silica gel 60 G on 1-m column (3-cm diameter) under pressure (0.2 kg/cm^2) with benzene/diethyl ether/hexane (90:10:5) as the eluent. HPLC analyses were performed on an LKB instrument equipped with a Brownlee Labs RP-18 Spheri (10 μm) column with a mixture of acetonitrile/water (70:30) as the eluent.

Photodimerization of Solid Ethyl (*E*)-α-Cyano-2-methoxycinnamate (1). Solid compound 1 (0.968 g) was deposited between two glass plates (20 × 20 cm) and irradiated for 4 h on each side with a mercury lamp (GEC 250 W) to give **2** as a colorless compound (0.918 g, 95% yield): mp 162–163 °C from ethanol (lit.[4] mp 162–163 °C); MS, *m/e* (relative intensity) 462 (3) (M$^+$, calcd 462), 231 (100, M$^+$/2), 200 (5), 172 (18). Alternatively, compound **2** was obtained on a large scale by sunlight irradiation of **1** as reported in ref 4.

(1α,2α,3β,4β)-1,3-Dicyano-2,4-bis(2-methoxyphenyl)cyclobutane-1,3-dicarboxylic Acid (3). Potassium hydroxide (1.2 g) in ethanol (20 mL) was added to compound **2** (2.3 g) dissolved in hot acetone (60 mL). The solution was stirred at 40–45 °C for 45 min, and a solid deposited, which was filtered and then dissolved in water (20 mL). Acidification of the solution with hydrochloric acid (0.5 M) gave the expected acid **3** (90% yield): mp 210–212 °C dec from ethanol/water (5:4); compound **3** crystallized with two molecules of water, which can be removed by heating near 140 °C; MS, *m/e* (relative intensity) 406 (0.4) (M$^+$, calcd 406), 362 (0.8, M$^+$ − CO$_2$), 318 (8, M$^+$ − 2CO$_2$), 203 (9, M$^+$/2), 159 (100). Anal. Calcd for $C_{22}H_{18}N_2O_6 \cdot 2H_2O$: C, 59.73; H, 5.01; N, 6.33. Found: C, 60.03; H, 4.95; N, 6.31.

Thermal Decarboxylation of (1α,2α,3β,4β)-1,3-Dicyano-2,4-bis(2-methoxyphenyl)cyclobutane-1,3-dicarboxylic Acid (3). Method A. Compound **3** (2 g) was deposited in a test tube equipped with a thermometer and was kept under nitrogen. The test tube was dipped in an oil bath at 180 °C, and the solid was allowed to warm up to 130–150 °C. When the inner temperature reached 195 °C, the sample softened and decarboxylation slowly occurred, giving rise to an orange-brown fluid. At this stage, the temperature of the mixture increased to 5–10 °C higher than that of the oil bath (thus suggesting that the reaction was exothermic). The reaction mixture was then heated at 205–210 °C for 3 min and allowed to cool. When the temperature in test tube reached 80–90 °C, two portions of ethanol (3 mL), were added to remove the reaction products. The mixture was left aside, and a solid separated, which was filtered and analyzed by TLC. By column chromatography of the above solid, five fractions were separated. Fraction 1 contained two products (TLC, benzene as eluent), which were recognized as a mixture of (*E*)- and (*Z*)-2-methoxycinnamonitriles (0.037 g) by ^{1}H and ^{13}C NMR spectra in comparison with those of authentic samples.[5] Evaporation of fractions 2, 3, and 4 left compounds **5** (0.345 g), **4** and **5** (0.182 g), and **4** (0.537 g). Fraction 5 separated a solid that was not studied further owing to the small quantity available (0.027 g). (1α,2α,3α,4β)-2,4-Bis(2-methoxyphenyl)cyclobutane-1,3-dinitrile (**4**): mp 144–145 °C (from ethanol); MS, *m/e* (relative intensity) 318 (18) (M$^+$, calcd 318), 159 (100, M$^+$/2). Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.34; H, 5.83; N, 8.57.

Compound **5**: mp 178–179 °C (from ethanol); MS, *m/e* (relative intensity) 318 (7) (M$^+$, calcd 318), 159 (100, M$^+$/2). Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.53; H, 5.67; N, 8.65.

Method B. Compound **3** (1 g) in diglyme (12 mL) was refluxed at 165–170 °C for 1 h. HPLC of the solid obtained after removal of the solvent (0.71) g) showed the presence of compounds **4** and **5**. Similar results were obtained when a solution of **3** (1 g) in dimethyl sulfoxide (11 mL) and water (0.5 mL) was heated at 175–180 °C for 1 h.

2,2′-Dimethoxy-α-truxillic Acid (7). Solid (*E*)-2-methoxycinnamic acid (**6**) (0.538 g) was deposited between two glass plates (40 × 40 cm) and irradiated with a mercury lamp (GEC 250 W) for 5 h on each side to give the dimer **7** (0.392 g, 73% yield): mp 262–263 °C (from AcOH). Alternatively, large quantities of compound **7** were obtained according to ref 1.

(1α,2α,3β,4β)-2,4-Bis(2-methoxyphenyl)cyclobutane-1,3-dicarbonyl Dichloride (8). 2,2′-Dimethoxy-α-truxillic acid (**7**) (1.5 g) was refluxed with thionyl chloride (20 mL) for 1 h. Evaporation of the excess thionyl chloride left **8** (95% yield), which was crystallized from benzene as colorless needles, mp 156–157 °C. Anal. Calcd for $C_{20}H_{18}Cl_2O_4$: C, 61.08; H, 4.58. Found: C, 61.52; H, 4.82.

(1α,2α,3β,4β)-2,4-Bis(2-methoxyphenyl)cyclobutane-1,3-dicarboxamide (9). Into a cooled solution of **8** (1 g) in benzene (60 mL) was bubbled ammonia to give a solid which was filtered and washed with saturated aqueous NaHCO$_3$. The crude diamide **9** (0.75 g) was crystallized from ethanol, mp 291–292 °C dec. Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.81; H, 6.36; N, 7.55.

(1α,2α,3β,4β)-2,4-Bis(2-methoxyphenyl)cyclobutane-1,3-dinitrile (5). Compound **9** (0.5 g) was refluxed with thionyl chloride (12 mL) for 1.5 h. Evaporation of the excess thionyl chloride left a solid (0.42 g) that was crystallized from ethanol to give **5** as a colorless compound, mp 178–179 °C (from ethanol; satisfactory analytical data), identical (TLC, ^{1}H and ^{13}C NMR, MS, and IR spectra) to that obtained by Method A or B.

Acknowledgment. We thank S. Papaleo for the elemental analyses.

Registry No. **1**, 14533-89-2; **2**, 109977-07-3; **2a**, 110043-36-2; **3**, 109977-08-4; **3a**, 110043-37-3; **4**, 109977-09-5; **5**, 110043-35-1; **6**, 1011-54-7; **7**, 94683-55-3; **8**, 109977-10-8; **9**, 109977-11-9; (*E*)-2-methoxycinnamonitrile, 57103-26-1; (*Z*)-2-methoxycinnamonitrile, 57103-24-9.

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(5) Unpublished results from this laboratory.

(6) Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.