Topochemistry. Part XVIII.* The Solid-state Photochemistry of some Heterocyclic Analogues of *trans*-Cinnamic Acid

By **M. Lahav** and **G. M. J. Schmidt**, Department of *X*-Ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel

β-2-Furylacrylic acid irradiated with λ > 290 mμ gives an oligomer of D.P. ~30 as well as dimer identified chemically and by its n.m.r. spectrum as the furyl analogue of β-truxinic acid. β-2-Thienylacrylic acid is dimorphic: its (thermodynamically) stable modification polymerises while the metastable form gives the β-truxinic dimer and small amounts of oligomer. 5-Methyl-2-thienylacrylic acid yields oligomer. β-3-Pyridylacrylic acid dimerises to the β-truxinic analogue; β-3-indolylacrylic acid is light-stable. According to the u.v. spectra all oligomers contain partially reduced ring systems.

The photo-behaviour of this series of compounds is interpreted in terms of the packing arrangement of the monomers and of the reactivity of the ring systems: the formation of β-truxinic dimers follows from the parallelism of monomers related by a 4 Å translation axis; polymerisation is initiated by the attack of photo-excited exocyclic >C=C< groups on sufficiently close double bonds of reactive (furan, thiophen) ring systems.

We have extended our work on the relation between crystal structure and solid-state photochemistry of the cinnamic acids [1] to some of their heterocyclic analogues in the hope of finding further packing patterns in β-substituted *trans*-acrylic acids and new reaction types. While the first aim was not realised we have, nevertheless, found examples of solid-state polymerisation in certain derivatives; [2] the present Paper describes the photochemistry of some compounds in the pyridine, furan, thiophen, and indole series. The photo-behaviour of the furan analogue of ω-nitrostyrene is also briefly reported.

EXPERIMENTAL

The *trans*-acrylic acids were prepared by condensation in pyridine solution of the appropriate aldehydes with freshly dried malonic acid. The nitro-compound was prepared by an adaptation of the method for ω-nitrostyrene.[3] The materials were crystallised from a series of solvents, and the powder patterns recorded on a " Guinier " Nonius camera with Cu K_α radiation. Irradiation by sunlight of powdered material was carried out in Petri dishes with Pyrex covers or in sealed evacuated Pyrex tubes; a Hanau Q81 lamp was also used in combination with the sealed tubes. The material was frequently shaken during irradiation and worked up when powder photographs taken at 2—3 days' intervals showed no further changes. Where the powder pattern of the monomer merely weakened but no new lines appeared different samples were exposed for varying periods of time and worked up separately.

trans-β-2-*Furylacrylic Acid* (I).—The acid was recrystallised from petroleum (b. p. 60—80°) to a colourless product of m. p. 140°; [4] recrystallisation from other solvents such as ethanol or benzene afforded a coloured product which, though of identical m. p., was considered unsuitable for photochemical work. Material exposed for 30 days to sunlight showed a continuous change in powder pattern. The sample was chromatographed on a thin layer of Kieselgel G, and the plate developed with benzene–methanol–acetic acid (45 : 8 : 4) [5] and exposed to iodine vapour which revealed three fractions: $R_f = 0$ (polymer), 0·47 (dimer), and 0·57 (monomer). Irradiated material (10·0 g.) was soxhleted with benzene; the hot solution deposited on cooling 5·1 g. of *dimer* (see below); a second fraction recovered from the cold benzene solution by evaporation consisted of pure monomer (I) identified by powder pattern, m. p., and mixed m. p. The benzene-insoluble fraction (2·4 g.), soluble in cold ethanol and in sodium hydroxide, did not give an *X*-ray pattern beyond a diffuse ring near 4 Å. Its molecular weight was determined in the ultracentrifuge by the multichannel method as 4000 ± 1000.[6] The u.v. spectrum of this oligomer is shown in Figure 1. Irradiation of the oligomer by sunlight caused further changes in the u.v. spectrum and loss of solubility in ethanol and in sodium hydroxide.

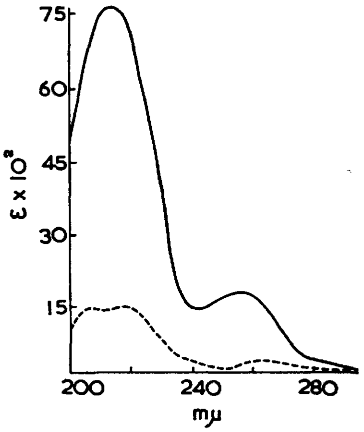


FIGURE 1 *trans*-β-2-Furylacrylic acid. Ultraviolet spectra (methanol) of dimer (II) ——, and of oligomer – – – –

Irradiation of monomer in evacuated tubes, *i.e.*, in the absence of atmospheric oxygen and moisture, gave the same dimer, as well as polymeric material.

trans-3,trans-4-*Di-2-furylcyclobutane*-1,cis-2-*dicarboxylic Acid* † (II).—M. p. 178—179° (from benzene) (Found: C, 60·8; H, 4·45. $C_{14}H_{12}O_6$ requires C, 60·85; H, 4·4%); $\lambda_{max.}$ (methanol) 2150 Å, ε 7640 (Figure 1). The mass

---

* Part XVII, S. Block, S. E. Filippakis, and G. M. J. Schmidt, preceding Paper.

[1] M. D. Cohen, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2000.

[2] F. L. Hirshfeld and G. M. J. Schmidt, *J. Polymer Sci.*, 1964, **2A**, 2181.

[3] A. P. Dunlop and F. N. Peters, " The Furans," Reinhold Publ. Co., New York, 1953, p. 168.

[4] E. C. Horning, *Org. Synth.*, Coll. Vol. III, 1955, p. 425.

[5] H. J. Petrowitz and G. Pastuska, *J. Chromatog.*, 1962, **7**, 128.

[6] D. A. Yphantis, *Ann. New York Acad. Sci.*, 1960, **88**, 586.

spectrum of the dimer included peaks at m/e 276 (molecular peak) and 138. The n.m.r. spectrum taken in deuterated dimethyl sulphoxide showed five peaks in the ratio 1 : 1 : 1 : 1 : 1 with τ 2·75 (hydrogen 5 of the furan ring), 3·90 (H 4), 4·10 (H 3), 6·10, and 6·40 (hydrogens 3 and 2 of the cyclobutane). The spectrum of the potassium salt, prepared by precipitation from methanol with potassium hydroxide (phenolphthalein), had τ 2·80 (doublet), 3·80 (quartet), 3·95 (doublet), 5·93 (multiplet), and 6·43 (multiplet); τ 5·30 (H_2O).

Treatment of compound (II) with dicyclohexyl-carbodiimide in chloroform, removal of the urea, and evaporation *in vacuo* of the solvent gave a material with $\nu_{max.}$ 1800 and 1860 cm.$^{-1}$ (five-membered cyclic anhydride). Ozonolysis of (II) (1·0 g.) in glacial acetic acid solution for 2 hr. at room temperature and treatment of the solution with 30% hydrogen peroxide for 48 hr. gave, after evaporation and treatment with diazomethane, the centrosymmetric tetramethoxycarbonylcyclobutane (III).[7]

trans-β-2-*Thienylacrylic Acid* (IV).—The acid, m. p. 147—148° [lit.,[8] 148°, from ethanol–water (1 : 1)], is dimorphic. The stable form (γ) can be prepared by slow crystallisation from hot solutions in nitromethane or aqueous ethanol. The metastable form (β) can be obtained by recrystallisation from hot benzene to a modification containing benzene of crystallisation, which in the open atmosphere rapidly loses benzene and turns into a powder of form β. Alternatively, large single crystals of (β) are formed by slow evaporation of solutions of compound (IV) in dimethylformamide. The transition temperature β ⟶ γ lies near 130° (microscope hot-stage), *i.e.*, higher than the temperature reached during irradiation with sunlight. The transformation also takes place by sublimation at normal temperature and pressure.

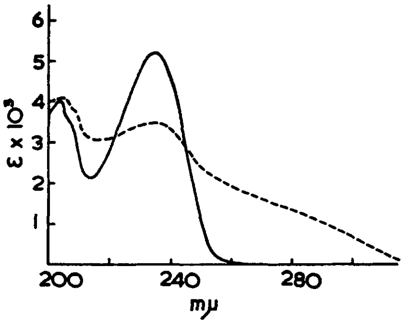
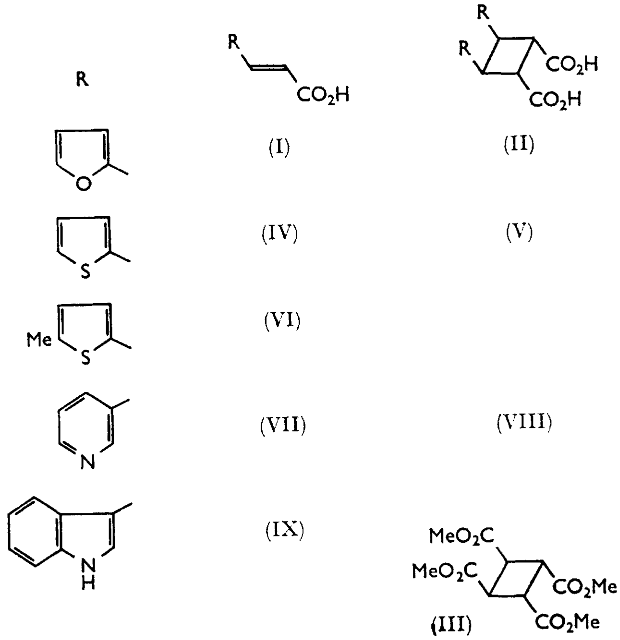


FIGURE 2 *trans*-β-2-Thienylacrylic acid. Ultraviolet spectra (methanol) of dimer (V) ——, and of oligomer - - - -

Irradiation of form γ in sunlight was carried out for 20 days. The material gradually acquired a dark brown colour; the powder pattern showed only a gradual weakening of the monomer lines. Similar results were obtained on material irradiated in evacuated Pyrex tubes. The thin-layer chromatogram (Kieselgel G) showed a material of R_f 0 and unchanged monomer (R_f 0·53). The entire material was soxhleted with benzene; an insoluble brown amorphous (X-ray pattern) material (20% yield) was separated from unconverted monomer (m. p., mixed m. p.). The average molecular weight of the oligomer determined in the ultracentrifuge by the multichannel method was 4000 ± 1000. The ultraviolet spectrum of the polymer is shown in Figure 2.

Irradiation of compound (IVβ) in sunlight produced within 5 days a complete change in powder pattern. The exposed material was soxhleted with benzene and an insignificant amount of brown residue discarded. The cold solution deposited a first crop of *dimer* (V) (see below); the mother-liquor was evaporated, and the residue fractionated with ethanol–water (1 : 1) into compounds (IV) and (V). The total yield of dimer amounted to 80%.

trans-3,trans-4-*Di*-2-*thienylcyclobutane*-1,cis-2-*dicarboxylic Acid* † (V).—M. p. 182—183° (benzene) (Found: C, 54·5; H, 3·9; S, 20·95. $C_{14}H_{12}O_4S_2$ requires C, 54·5; H, 3·9; S, 20·8%). On treatment with boiling acetic anhydride the title compound (V) gave a compound with $\nu_{max.}$ 1780 and 1860 cm.$^{-1}$. The dimer in methanol (Figure 2) had $\lambda_{max.}$ 203 mμ (ε 1155), 206 (ε 885), and 236 (ε 1655). The n.m.r. spectrum (deuterated dimethyl sulphoxide) showed peaks at τ = 2·85, 3·20, 5·75, and 6·40 in the ratio 1 : 2 : 1 : 1.



trans-β-(5-*Methyl*-2-*thienyl*)*acrylic Acid* (VI).—M. p. 162° [lit.,[8] 162° (ethanol)]. Irradiation in sunlight for 4 days produced a broadening of the powder pattern of the monomer; 3·0 g. of compound (VI) yielded 0·5 g. of polymer insoluble in benzene; no other photo-products were observed. The u.v. spectrum (ethanol) of the polymer had $\lambda_{max.}$ 202 and 250 mμ.

trans-β-3-*Pyridylacrylic Acid* (VII).—12·4 g. of acid recrystallised from ethanol [m. p. 233° (decomp.), lit.,[9] m. p. 233°] was irradiated under Pyrex for 30 days in sunlight. The material was soxhleted with dioxan, and 7·6 g. of dimer obtained.

trans-3,trans-4-*Di*-3-*pyridylcyclobutane*-1,cis-2-*dicarboxylic Acid* † (VIII).—The material, which probably contains solvent of crystallisation, decomposes between 180 and 210° depending on the rate of heating. The analytical

---

† *Note.*—In the names of structures (II), (V), (VIII), etc., the stereochemistry is related to the carboxy-group numbered 1. ED.

[7] G. W. Griffin, A. F. Vellturo, and K. Furukawa, *J. Amer. Chem. Soc.*, 1961, **83**, 2725.

[8] W. J. King and F. F. Nord, *J. Org. Chem.*, 1949, **14**, 405.

[9] A. Dornow and W. Schacht, *Chem. Ber.*, 1947, **80**, 505.

sample (dioxan–water) was dried at 90°/10^{-3} mm. for 3 days (Found: C, 64·45; H, 4·8; N, 9·25. $C_{16}H_{14}N_2O_4$ requires C, 64·4; H, 4·75; N, 9·4%). The u.v. spectrum (ethanol) had $\lambda_{max.}$ 258 mμ (ε 1850), 263 (ε 2000), and 270 (ε 1550). The n.m.r. spectrum (in D_2O) of the dipotassium salt, prepared by titration with methanolic KOH (phenolphthalein) and precipitated with excess of ether, had τ 2·00 (doublet, hydrogen 2 and 6 of the pyridine ring), 2·60 (multiplet, hydrogen 5), 3·00 (multiplet, hydrogen 4), 4·75, 6·35 (multiplets, cyclobutane hydrogens) in the ratio 2 : 1 : 1 : 1 : 1; τ (H_2O) 5·30. The i.r. spectrum of the anhydride had $\nu_{max.}$ 1790 and 1860 $cm.^{-1}$.

trans-β-3-*Indolylacrylic Acid* (IX).—Commercial material (Fluka, purum) recrystallised from ethanol, m. p. 187—188° (lit., 191—193°,[10] 180° [11]) was exposed to sunlight under cellophane for 27 days. No changes in m. p. or powder diagram could be observed.

1-2′-*Furyl-2-nitroethylene* (X).—The compound was prepared by condensation of furfural with nitromethane in ethanolic sodium hydroxide;[3] the compound (m. p. 75°, lit.,[3] 74—75°) is dimorphic; the stable form (*A*) is obtained as long prisms from methylcyclohexane, the metastable form (*B*) as laths by sublimation at 25°/25 mm. (X, *B*) is completely polymerised in the solid state by irradiation with sunlight in a matter of several hours. It is equally sensitive to *X*-rays (Cu K_α radiation) since single crystals irradiated for 20 hr. no longer give a recognisable diffraction pattern though they have kept their shape intact and surfaces clear.

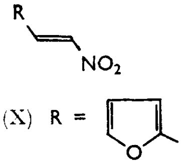
Form *A* irradiated by sunlight for 4 days at 20° (when sublimation is suppressed) forms a (crystalline) *photo-product* (see below) which was extracted from the mixture with ethanol.

Di-2-furyldinitrocyclobutane. M. p. 140—141° (ethanol–acetone) (Found: C, 51·55; H, 3·85; N, 9·8. $C_{12}H_{10}N_2O_6$ requires C, 51·8; H, 3·6; N, 10·05%); $\nu_{max.}$ 1570 and 1360 $cm.^{-1}$, observed in secondary nitro-compounds; 723, 750, 821, 887, 1030 $cm.^{-1}$, characteristic of the furan group. The maxima at 955 and 970 $cm.^{-1}$ of the monomer (exocyclic *trans* $>C=C<$ group) are absent. The u.v. spectrum had $\lambda_{max.}$ (EtOH) 204 and 257 mμ; the spectrum changed gradually, and the compound evidently underwent an irreversible reaction in ethanol. The mass spectrum showed peaks at *m*/*e* = 278 and 139.

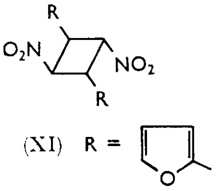
RESULTS

Dimers.—The structure of the photo-dimer (II) of furylacrylic acid as the β-truxinic-acid analogue follows from the formation of a five-membered cyclic acid anhydride, and the ozonolysis of (II) to a cyclobutanetetracarboxylic acid, identified after esterification as the tetramethyl ester (III), the solid-state photo-dimer of dimethyl fumarate. The n.m.r. spectrum of the cyclobutane corresponds to the A_2X_2 type already observed by Steinmetz *et al.*[12] in one of the isomeric dichlorocyclobutanedicarboxylic acids, and by Krauch *et al.*[13] in β-truxinic acid. The dimers from thienyl- and pyridyl-acrylic acids also give five-membered cyclic acid anhydrides; hence the two carboxyl groups are attached *cis*-1,2 to the cyclobutane rings. The n.m.r. spectra of compounds (V) and (VIII) are also of the A_2X_2 type and hence the 3,4-*trans*-attachment is ruled out absolutely by the symmetry of the spectrum; the similarities of the spectra of the compounds reported here and in the Papers just quoted [12,13] make their assignments as β-truxinic type highly probable. A detailed analysis of the n.m.r. spectra of these compounds will be reported later.

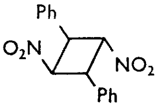
The structure of the photo-product from furylnitroethylene as cyclobutane dimer follows from the molecular peak and the peak *m*/*e* = 139, corresponding to the monomer; this split has been shown by Mandelbaum [14] to be characteristic of the cyclobutanes from cinnamic acids, chalcones, and butadienes. The disappearance, in the i.r. spectrum of the dimer, of the bands at 955 and 970 $cm.^{-1}$ characteristic of the *trans*-substituted exocyclic double bond of the monomer, and the shifts of the bands at 1320 and 1490 $cm.^{-1}$ in the monomer (nitro-group attached to conjugated system) to 1360 and 1570 $cm.^{-1}$ (observed in secondary nitro-groups) support this structure assignment. In view of the instability of the dimer in solution, as indicated by changes of its u.v. spectrum with time, the n.m.r. spectrum could not be measured. We believe that the dimer has the centrosymmetric configuration (XI), in view of the similarity of the cell constants of the monomer (*a* = 9·17, *b* = 5·32, *c* = 15·31 Å, β = 120·0°; space group $P2_1/c$) with those of ω-nitrostyrene (*a* = 8·28, *b* = 5·80, *c* = 18·24 Å, β = 115·2°; space group $P2_1/c$); the latter is known to give the centrosymmetric dimer (XII).[15]



(X)



(XI)



(XII)

Oligomers.—The u.v. spectra, based on equivalent concentration relative to monomer, of the oligomer from compound (I) and of the cyclobutane dimer (II) are shown in Figure 1. The peak at 215 mμ characteristic of α-alkyl substituted furans (*e.g.*, 2-methylfuran [16]) is seen in both photo-products, although it is considerably lower in the oligomer. We would assign the second peak at 205 mμ to a vinylether group [17] or to an αβ-unsaturated carboxyl group. The spectra of the oligomer and the dimer of compound (IV) are shown in Figure 2. The peaks of the dimer (V) at 203, 206, and 236 mμ can be assigned to 2-alkyl-substituted thiophens; in the oligomer the relative intensities of the two principal maxima are inverted, and a broad band appears in the region 260—300 mμ. The decrease in the 236 mμ band argues for partial disappearance of the thiophen group and the appearance of a $>C=\overset{|}{C}-S$ group and/or an αβ-unsaturated acid. The spectrum of the oligomer from the 5-methyl derivative (VI) shows a similar system of maxima; the shift of the wavelength peak by 14 mμ to 250 mμ argues for the partial preservation of the heterocyclic ring during polymerisation.

---

[10] J. S. Moffatt, *J. Chem. Soc.*, 1957, 1442.

[11] J. M. Kaper, O. Gebhard, C. J. van den Berg, and H. Veldstra, *Arch. Biochem. Biophys.*, 1963, **103**, 469.

[12] R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, 1965, **98**, 3854.

[13] C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, 1966, **99**, 625.

[14] A. Mandelbaum, private communication.

[15] D. B. Miller, *Diss. Abs.*, 1958, **18**, 1981.

[16] H. L. Rice, *J. Amer. Chem. Soc.*, 1952, **74**, 3193.

[17] G. Eglington, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1952, 2873.

DISCUSSION

The cell dimensions of the acids referred to in this Paper are listed in Table 1. According to their shortest axes the crystal structures of (I), (IV β), and (VII)

TABLE 1

Crystallographic constants of some heterocyclic analogues of cinnamic acid

		a (Å)	b (Å)	c (Å)	β (°)	Space group	n
2-Furyl	β	18·98	3·84	20·13	113·9	$C2/c$	8
2-Thienyl A	γ	11·41	5·04	13·08	98·2	$P2_1/c$	4
B	β	9·59	3·91	20·19	109·5	$P2_1/c$	4
5-Methyl-2-thienyl		10·9	21·3	7·2	104·0	$P2_1/c$	8
3-Pyridyl	β	3·84	16·03	11·64	91·0	$P2_1/c$	4
2-Indolyl	γ	14·9	5·1	12·8	95·0	$P2_1/c$	4

belong to the β-type, while (IV γ) and (IX) are γ-modifications.[18] The correctness of this assignment is also seen by a comparison of the packing diagrams of (I) [19] and (IV β) (preceding Paper), shown in Figures 3 and 4, with that of *p*-chlorocinnamic acid (Figure 1, Part III [18]), and of (IV γ) [19] (Figure 5) with that of the γ-modification of *m*-chlorocinnamic acid (Figure 3, Part III). The β-structures show the same short contacts of the exocyclic double bonds along the 4 Å axis; second nearest-neighbour contacts of these groups have shrunk from >5 Å in the cinnamic series to 4·8 and 4·5 Å (across screw axes in the thienyl derivative, and centres of symmetry in the furyl acid) as a result of the successive reduction in size

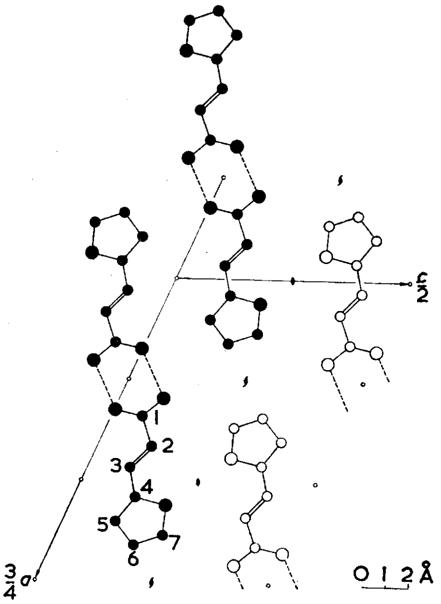


FIGURE 3 *trans*-β-2-Furylacrylic acid. Packing arrangement seen along [010]

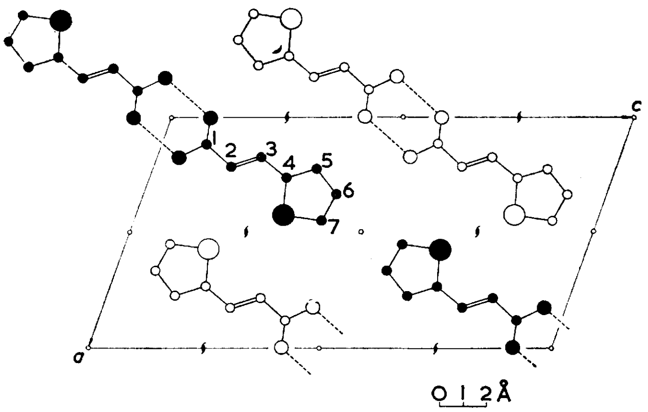


FIGURE 4 *trans*-β-2-Thienylacrylic acid, form (IVβ). Packing arrangement seen along [010]

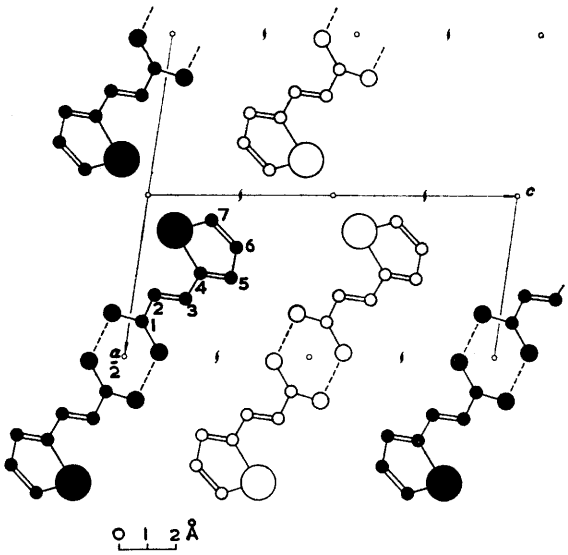


FIGURE 5*a* *trans*-β-2-Thienylacrylic acid, form (IVγ). Packing arrangement seen along [010]

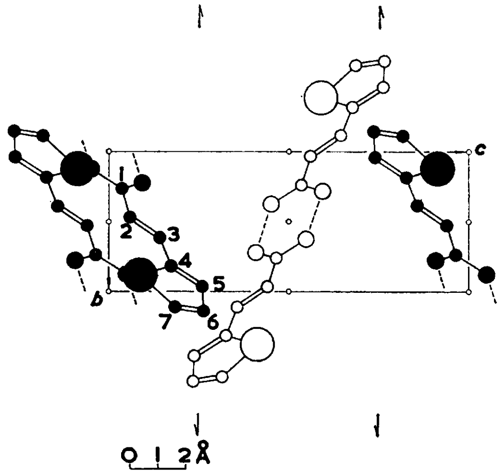


FIGURE 5*b* *trans*-β-2-Thienylacrylic acid, form (IVγ). Packing arrangement seen along [100]

---

[18] G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2014.

[19] Part XVI, S. E. Filippakis and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1967, 229.

of the ring. In the γ-type the shortest contact of exocyclic >C=C< groups is provided by the 5·0 Å translation axis. In accordance, again, with these crystallographic classifications is the formation of β-truxinic acid analogues from (I), (IV β), and (VII), and the total absence of a cyclobutane from the γ-form of (IV) and from (IX). We may therefore conclude that the *dimerisation* reaction of the cinnamic acid analogues studied here follows the topochemical rules established for the phenyl derivatives.

The novel features presented by the furan and thiophen derivatives is the formation of oligomers in which, according to the spectroscopic evidence, the ring systems are partially reduced and have therefore taken part in the polymerisation reaction. We propose that in these two series attack of a photo-excited exocyclic >C=C< group on one of the double bonds of the ring leads to the formation of a dimer diradical which cannot ring-close in a termination reaction (characteristic of cyclobutane formation) but leads instead to propagation by further reaction of either end of this diradical with other neighbouring >C=C< groups. The short contacts (3·4 Å and up) between endocyclic and exocyclic double bonds required for the reaction initiating polymerisation, *i.e.*, for the formation of the dimer diradical, are indeed observed in the γ-modification of thienylacrylic acid (Table 2). In the β-types these short contacts are invariably present within each stack along the 4 Å axis (Table 3*a*, *b*) so that in sufficiently reactive ring-systems polymerisation, by the mechanism postulated here, should accompany dimerisation. This dual reaction path is indeed followed in the furan derivative; the small yield of oligomer accompanying dimer in the photoreaction of (IV β) may be due to kinetic factors connected with lower reactivity of the thiophen compared with the furan system.

TABLE 2

Intermolecular contacts (<4·3 Å) between carbon atoms of exocyclic and endocyclic >C=C< groups in thienylacrylic acid, γ-form

A_{000} *	$A_{0\bar{1}0}$		A_{000}	$\bar{B}_{000}$	
C(2) †	C(4)	3·73 Å	C(6)	C(7)	3·76
C(2)	C(5)	3·74	C(7)	C(7)	3·69
C(2)	C(6)	3·71			
C(2)	C(7)	3·73		$B_{0\bar{1}0}$	
C(3)	C(4)	4·15	C(6)	C(7)	3·96
C(3)	C(5)	3·72	C(7)	C(7)	3·69
C(3)	C(6)	3·49			
C(3)	C(7)	3·85		$\bar{B}_{01\bar{1}}$	
C(4)	C(6)	3·74	C(2)	C(5)	3·88
C(4)	C(7)	4·02	C(2)	C(6)	4·03
C(5)	C(6)	4·27			

* Co-ordinates of equivalent positions	Symbol
xyz	A
$\bar{x}\bar{y}\bar{z}$	$\bar{A}$
$\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$	B
$x, \frac{1}{2} - y, \frac{1}{2} + z$	$\bar{B}$

A_{pqr} denotes fractional co-ordinates $p + x, q + y, r + z$.
† For numbering of atoms see Figure 5.

We wish to stress three results emerging from the work presented here: first, in the systems investigated the molecular packing arrangement controls reaction types, namely dimerisation and polymerisation. The effect is demonstrated unambiguously by the two crystal forms of thienylacrylic acid and of 1-2′-furyl-2-nitroethylene. Secondly, polymerisation which in three compounds leads to low-molecular-weight products (D.P. ~20) is initiated in the crystalline phase at temperatures well below the m. p. of the monomers. We therefore can see no need to invoke, in these compounds at any rate, the need for, or the role of, imperfections or dislocations in the primary step. (We cannot of course discuss the sequence of events following upon formation of the dimer diradical from the crystallographic evidence alone.) Thirdly, as an extension of this second point, we believe that the geometrical proximity of reactive centres is as essential a prerequisite for the initiation of polymerisation as it has been proved to be for cyclodimerisation. This last point cannot be said to have been proved conclusively since we have not yet found a light-stable derivative in this series of compounds. Indeed, their complex photochemical behaviour as trienic systems suggests that further investigations are likely not to be rewarding, and we have consequently turned to the photochemistry of butadiene derivatives which will be reported in further Papers.

TABLE 3

Intrastack contacts (<4·3 Å) between carbon atoms of exocyclic and endocyclic >C=C< groups in two β-packing types

a Furylacrylic acid			*b* Thienylacrylic acid, β-form		
A_{000} *	A_{010}		A_{000}	A_{010}	
C(6) †	C(7)	4·03 Å	C(2) ‡	C(3)	3·73 Å
			C(4)	C(5)	3·79
	$A_{0\bar{1}0}$				
C(2)	C(3)	3·75		$A_{0\bar{1}0}$	
C(2)	C(4)	3·71	C(3)	C(4)	3·96
C(3)	C(4)	3·49	C(4)	C(7)	4·14
C(3)	C(5)	3·75	C(5)	C(6)	3·83
C(3)	C(6)	4·10	C(5)	C(7)	3·69
C(3)	C(7)	4·05	C(6)	C(7)	3·57
C(4)	C(5)	3·75			
C(4)	C(6)	3·61			
C(4)	C(7)	3·62			
C(5)	C(6)	3·55			
C(5)	C(7)	3·96			
C(6)	C(7)	4·10			
	$\bar{A}_{010}$				
C(3)	C(5)	4·01			

* For definition of symbols see Table 2. † For numbering of atoms see Figure 3. ‡ For numbering of atoms see Figure 4.

We thank Dr. A. Mandelbaum of the Chemistry Department, Technion, Haifa, for his mass-spectrometric measurements, and Mr. A. Lustig of the Biophysics Department, Weizmann Institute, for molecular weight determinations in the ultracentrifuge. We also acknowledge support from the National Bureau of Standards, Washington, D.C.

[6/658 *Received, May* 31*st*, 1966]