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## Topochemistry. Part XXIII.<sup>1</sup> The Solid-state Photochemistry at 25° of Some Muconic Acid Derivatives

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trans, trans-Muconic acid, its monomethyl ester, and cis, cis-isomer, all of which crystallise in cells with shortest axes of 4 Å, react in the solid state on irradiation with  $\lambda > 290$  m $\mu$ . At room temperature all give vinyl-substituted cyclobutanes of symmetry m, the configuration of which reproduces the geometry of the monomer molecules both in the attachment of the ring substituents and in the configuration of the vinyl side-chain. The all-trans-acid and its monomethyl ester give, in addition to dimers, various amounts of oligomers which, according to the spectroscopic evidence, are formed by both 1,4- and 1,2-addition of the butadiene chains. Dimethyl trans, trans-muconate, which does not crystallise in a 4 Å cell, is stable to  $\lambda > 290$  m $\mu$  at 25°.

In continuation of our work on the lattice control of photochemically initiated solid-state polymerisation,<sup>2,3</sup> we now report on the photochemical behaviour of derivatives of muconic acid, including trans, trans-muconic acid (I),<sup>4</sup> its monomethyl ester (II),<sup>5</sup> cis,cis-muconic acid (III),6 and dimethyl trans, trans-muconate (IV).1 All, except the last, occur in crystal structures having a shortest axis of 4 Å ( $\beta$ -type in our nomenclature), and are thus crystallographically homologous with monoand di-methyl fumarate.<sup>7</sup> The solid-state photochemistry of trans, trans-muconodinitrile<sup>8</sup> and sorbic acid,<sup>9</sup> which also crystallise in the  $\beta$ -packing type, will be reported later.

The formation of cyclic dimers would be expected from the short axis packing type, though whether cyclooctadienes and/or divinyl-substituted cyclobutanes would be formed was an open question which the present investigation also sought to answer.

#### EXPERIMENTAL

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Infrared spectra were taken in KBr (unless otherwise stated). Ultraviolet spectra were measured on a Unicam SP 700, and n.m.r. spectra on a Varian A60.

Molecular weights of the oligomers were measured by the multichannel technique,<sup>10</sup> on the ultracentrifuge of the Biophysics Department of the Weizmann Institute, by Mr. A. Lustig. Anhydrisation of dicarboxylic acids was carried out with dicyclohexylcarbodi-imide in methylene chloride-ether (1:1) at room temperature. Ozonolysis was effected in glacial acetic acid and followed by treatment at room temperature for 48 hr. with 30% hydrogen peroxide; the excess of hydrogen peroxide was destroyed with hot palladised charcoal, and the solvent removed by evaporation. Mass spectra were measured by Dr. A. Mandelbaum of the Chemistry Department, Technion, Haifa, on an Atlas CH4.

trans, trans-Muconic Acid (I).-Three samples of the acid [Fluka purum, m. p. 295° (decomp.), modification from

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<sup>5</sup> Part XIX, D. Rabinovich and G. M. J. Schmidt, J. Chem. Soc. (B), 1967, 286.

ethanol or acetic acid] were irradiated for 16, 30, and 47 days in sunlight under Cellophane. The monomer was also irradiated, in sealed Pyrex vessels which had previously been evacuated and then filled with (tank) nitrogen, with a Hanau Q81 lamp. Material exposed in air compacted and became brown; both effects were absent in samples irradiated under nitrogen, primarily because of the exclusion of moisture. Powder photographs taken at 5-day intervals showed the broadening of the pattern of (I) and the appearance of a few additional lines. Ultraviolet spectra of the mixture taken after 30 days' irradiation showed a lowering of the maximum of the monomer at 266 and a new peak at 212-213 mµ. Thin-layer chromatography of this material with ammonia-water-methanol<sup>11</sup> gave three peaks of  $R_f 0.56$ , 0.40, and 0. Material (5.0 g.) exposed for 30 days was thoroughly stirred with cold methanol, and unchanged monomer filtered from the light brown solution; the filtrate was evaporated to dryness at  $0^{\circ}/3$  mm., the highly hygroscopic solid dissolved in a minimum of butanol, and this solution chromatographed <sup>12</sup> over silicic acid (Mallinckrodt; 100 mesh). The dimer was eluted with chloroform-n-butanol, and the solvent evaporated  $(0^{\circ}/3 \text{ mm.})$ ; the polymer which had remained on the column was extracted with methanol. Alternatively, the mixture was esterified at 0° with diazomethane, and chromatographed on a column of silicic acid with chloroform.

The yield of dimer (18-26%), depending upon the length of irradiation) can probably be increased by more appropriate irradiation techniques; in the present work we chose to interrupt the reaction after low conversion since the powder photographs indicated progressive disordering of the monomer phase, and we wished to exclude possible sidereactions in the non-crystalline regions.

trans-3, trans-4-Dicarboxy-1, cis-2-cyclobutanedi(transacrylic Acid) (V).\*-The compound, which decomposes when heated, is strongly hygroscopic and unsuitable for analysis. The sodium salt was prepared by precipitation from the dimer dissolved in methanol, taken up in water, and converted into the tetrasilver salt by treatment with silver nitrate solution (Found: C, 20.6, 19.6; H, 1.7, 1.3. C12H8Ag4O8

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<sup>7</sup> Part III, G. M. J. Schmidt, J. Chem. Soc., 1964, 2014.
<sup>8</sup> Part XXI, S. E. Filippakis, L. Leiserowitz, and G. M. J. Schmidt, J. Chem. Soc. (B), 1967, 297.
<sup>9</sup> J. M. Robertson and S. A. Sutherland, personal com-

munication.

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<sup>\*</sup> Note.-In the names of substituted cyclobutanes the stereochemistry is related to the group at position 1.--ED.

requires C, 20.15; H, 1.4%). The mass spectrum indicated rearrangement to a cyclo-octadienetetracarboxylic acid [as (VI)].  $v_{max}$  of (V) 1700 (carboxyl), 1690 ( $\alpha\beta$ -unsaturated acid), 1651 and 980 cm.<sup>-1</sup> (trans-substituted double bond);  $\lambda_{max}$ . (H<sub>2</sub>O) 212 mµ (the spectrum gradually changes at room temperature; Cope rearrangement). The n.m.r. spectrum (D<sub>2</sub>O) showed a multiplet near  $\tau$  3.9, a doublet near 4.8  $(H_{\beta} \text{ and } H_{\alpha}, \text{ respectively, of the side-chain})$  with a coupling constant of 18 c./sec., and peaks at 6.2 and 6.8 (H-1 and H-3 of the cyclobutane ring) in the ratio 1:1:1:1. The coupling constant corresponds to the trans configuration of the hydrogens of the exocyclic double bond. The spectrum was calibrated with tetramethylsilane as external standard. The dimer was anhydrised with dicyclohexylcarbodi-imide at 0° (to prevent the Cope rearrangement), the substituted urea filtered off, the filtrate evaporated, and the solid residue (quantitative yield) dried  $(P_2O_5)$ ; 1860 and 1790 (five-membered cyclic anhydride), 1700 cm.<sup>-1</sup> (carboxyl). The persistence of the 980 cm.<sup>-1</sup> band and the absence of a maximum at 700 cm.<sup>-1</sup> indicate the presence of the trans-substituted, and the absence of a cis-substituted, double bond in the anhydride.

Ozonolysis of the acid (V) (1.0 g.) was carried out as described above; the crystalline residue obtained after removal of the solvent was esterified with diazomethane; the product (0.43 g., 44%) was recrystallised from benzene and identified by m. p. (144-145°), mixed m. p., and X-ray powder photographs as the centrosymmetric ester (VII).<sup>13</sup> Ozonolysis of the tetraester (VIII) (0.1 g.) led to an oily residue (0.02 g) which was dissolved in acetone and dried in a vacuum. After several days it yielded crystals whose powder photograph was identical with that of the dimer of monomethyl fumarate (IX).14

The polymer (1-2% yield) showed no evidence of crystallinity in its X-ray diagram; the infrared spectrum had broad maxima near 1700 and 960–980 cm.<sup>-1</sup>;  $\lambda_{max}(H_2O)$ 205, 212 mµ. The molecular weight of the esterified (diazomethane) product, measured at three concentrations (0.5, 0.75, and 1% in dimethylformamide solution), was  $5400 \pm 700.$ 

Methyl Hydrogen trans, trans-Muconate (II).-Prepared by partial hydrolysis of (IV) according to Karrer and Stoll,<sup>15</sup> the product (m. p. 163°, 163° 15) was recrystallised from benzene, and irradiated in sunlight under Cellophane in air, in evacuated sealed Pyrex bulbs (5 days), and under a Hanau Q81 lamp through Cellophane (30 days). The samples which were open to the atmosphere turned brown whilst the material exposed in a vacuum remained colourless. The powder lines of the monomer broadened during irradiation; the progressive destruction of the crystalline regions was indicated also by a gradual change of the original, free-flowing material to a sticky product, an effect which was noticeable even in the evacuated tubes. Irradiation was therefore interrupted after a low degree of chemical conversion. Thin-layer chromatography of all samples with benzene-methanol-acetic acid (45:8:4)<sup>16</sup> gave optimal separation into four spots  $[R_f = 0, 0.36, 0.44, and 0.54]$ (monomer)]. The exposed material was treated with cold ether (containing a small amount of quinol), in which the polymer was insoluble; the ether solution was evaporated in vacuo, and the residue chromatographed; two of the

three components were separated on Kieselgel H with benzene-methanol-acetic acid (45:8:4) under 1.5 atm. pressure; one of these was identified as the monomer.

The ether solution containing all products except the polymer was treated with diazomethane, and the esterified material chromatographed; only two spots were now



obtained, which had  $R_{f}$  values identical with those of dimethyl muconate (IV) and the tetraester (VIII). This comparison of  $R_{\rm f}$  values was carried out with various chloroform-acetone mixtures.

trans-3, trans-4-Dimethoxycarbonyl-1, cis-2-cyclobutanedi-(trans-acrylic Acid) (X).-Obtained from the Kieselgel H column (7% yield), the compound, after evaporation of the solvent, was a hygroscopic oil which solidified on standing. The silver salt was prepared through the barium salt (Found : C, 31.75; H, 2.75. C<sub>14</sub>H<sub>14</sub>Ag<sub>2</sub>O<sub>3</sub> requires C, 31.95; H, 2.7%). The infrared spectrum (chloroform) had a broad peak near 1700-1725 cm.-1 [non-conjugated acid and conjugated ester groups (1700 and 1717-1730)], and  $v_{max}$ . 1651 and 975 cm.<sup>-1</sup> (trans-substituted double bond). The n.m.r. spectrum (CDCl<sub>3</sub>; tetramethylsilane as standard) had  $\tau 3.1$  (multiplet), 4.0 (doublet), 6.25 (singlet) overlapping a peak near 6.55, in the ratio 1:1:5. Anhydrisation of (X) with dicyclohexylcarbodi-imide gave a compound with  $v_{max}$  1860, 1790 cm.<sup>-1</sup> (five-membered cyclic anhydride),

<sup>15</sup> P. Karrer and M. Stoll, Helv. Chim. Acta, 1931, 14, 1189.

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and a sharp peak at 1725 cm.<sup>-1</sup> (aβ-unsaturated methoxycarbonyl). The band at 1700 cm.<sup>-1</sup> present in (X) was now absent, and the bands at 1651 and 975  $\rm cm.^{-1}$  persisted. (X) was esterified with diazomethane, and the resulting product identified again with the tetraester (VIII).

The dimer of  $R_{\rm f}$  0.44 could not be extracted from the Kieselgel H column, probably because it rearranged during elution. It was taken from the thin-layer chromatogram by extraction with cold ethanol;  $\lambda_{max}$  220 m $\mu$  which decreased on heating when a new band appeared at 206 m $\mu$ (Cope rearrangement).\*

The ether-insoluble fraction (21%) of the material irradiated in a vacuum was esterified with diazomethane; the molecular weight, determined at three concentrations (0.4,0.8, and 1.6%) in dimethylformamide solution, was  $15,000 \pm$ 3000. The ultraviolet spectrum of the original oligomer is shown in Figure 1; the infrared spectrum had broad maxima near 1700-1750 and 965-976 cm.-1.



FIGURE 1 Ultraviolet spectrum of solid-state oligomer from monomethyl trans, trans-muconate. (1 mg. of oligomer in 50 c.c. of methanol; 1-cm. cell)

cis,cis-Muconic Acid (III).-The compound [prepared by peracetic acid oxidation of phenol; 17 m. p. 186° (methanol)] (5.0 g.) was irradiated in sunlight under Cellophane for 6 days; powder photographs taken every 2 days showed the rapid appearance of a new set of lines and the disappearance of the monomer pattern. The m. p. of the sample decreased progressively during irradiation. Thin-layer chromatography <sup>11</sup> of the irradiated sample gave two peaks,  $R_{\rm F}$  0.54 (monomer) and 0.38 (dimer). The irradiated sample was stirred with methanol, and the monomer (powder pattern) filtered off. Evaporation of the solvent at 25°/ 3 mm. gave colourless crystalline material (3.5 g.) whose powder pattern did not correspond to that of the compound formed in the solid-state photo-reaction (polymorphism of the dimer; second form possibly solvated). A second sample irradiated under identical condition for 14 days gave 80% dimer.

### cis-3, cis-4-Dicarboxy-1, cis-2-cyclobutanedi-(cis-acrylic

Acid) (XI) .--- The compound was hygroscopic and unsuitable for analysis. The sodium salt was prepared by precipitation from the dimer dissolved in methanol, taken up in water, and converted into the tetrasilver salt (Found: C, 20.2; H, 1.4. C<sub>12</sub>H<sub>8</sub>Ag<sub>4</sub>O<sub>8</sub> requires C, 20.15; H, 1.4%). The mass spectrum of (XI) indicated conversion into a cyclo-octadienetetracarboxylic acid [as (VI)].  $\nu_{max}$  of (XI) 820 (cis-substituted CH=C-C=O),<sup>18</sup> and 1640 and 1690 cm.<sup>-1</sup>,

 $\lambda_{max}$  (H<sub>2</sub>O) 210 mµ (cis-substituted C=C-CO<sub>2</sub>H). (XI) was anhydrised with carbodi-imide; the product had  $v_{max}$  1860, 1790, 1965, 1639, 820 cm.<sup>-1</sup> (five-membered cyclic anhydride and cis-substituted CH=C-CO<sub>2</sub>H group).

Ozonolysis of (XI) (1.0 g.), followed by esterification with diazomethane, and recrystallisation from xylene (38%), gave a product, m. p. 203-204° (XII) identical with an authentic specimen of tetramethyl all-cis-cyclobutanetetracarboxylate.19

The tetramethyl ester of (XI) was prepared with diazomethane. The n.m.r. spectra of (XI) and its tetramethyl ester were taken in perdeuterioacetone and in deuteriochloroform (with tetramethylsilane as reference compound), respectively. The spectrum of (XI) showed a multiplet near  $\tau$  3.4, a doublet at 4.14 (H<sub>a</sub> and H<sub>b</sub>, respectively, of the side-chain) with separation of 12 c./sec., multiplets near  $5\cdot 2$  and  $6\cdot 2$  (H-2 and H-4 of the cyclobutane ring), in the ration 1:1:1:1. The spectrum of the tetraester showed a multiplet near  $\tau$  3.5, a doublet near 4.15 (with separation of 12 c./sec), and two singlets, overlapping the peaks of the methyl group, at 6.32 and 6.58, in the ratio 1:1:8. The splitting of the doublets corresponds to the cis-configuration of the hydrogens in the side-chain [cf. 18 c./sec. in the dimer of trans, trans-muconic acid (V)].

Dimethyl trans, trans-Muconate (IV) .--- The compound, prepared from muconic acid and methanolic hydrochloric acid, had m. p. 156° (lit., 20 156°). It was irradiated with a Hanau Q81 lamp through Pyrex for 6 weeks; no change could be observed in the m. p. or the X-ray powder photograph. Thin-layer chromatography did not reveal any photoproducts.

#### RESULTS

With the exception of dimethyl trans, trans-muconate, all compounds reported here dimerise at  $\lambda > 290$  mµ. The light-stability of (IV) under conditions of irradiation which cause the dimerisation of (II) cannot be explained in terms of differences in the absorption spectra of the two compounds; we have measured the transmission of thin films of the two esters (II) and (IV) (Figure 2), and find, as expected, very similar absorption spectra in the end-absorption region above 300 mµ.

The all-cis-acid gives the cyclobutane (XI) in 80% yield after 14 days in local sunlight; the observation 21 that the acid " was unchanged by exposure to daylight (4-5 weeks) " in London reflects more on the respective climatic conditions than on the photo-properties of the acid. The configuration of (XI) has been established as follows: the cisconfiguration of the carboxyl group attached to the ring follows from the formation of a five-membered cyclic anhydride; the all-cis configuration of the ring substituents has been established by ozonolysis of (XI) followed by esterification to the all-cis-ester (XII) previously obtained 19 from the cis-dimer of acenaphthylene by ozonolysis and subsequent methylation. The cis configuration of each of two acrylic-acid side-chains could be established from the infrared and n.m.r. spectra.

The structure of the trans-acid dimer (V) is based on ozonolysis and esterification to the (centrosymmetric) tetraester (VII) identical with the solid-state photodimer of

<sup>\*</sup>  $\lambda_{max}$  of material directly taken from the thin-layer chromatogram is red-shifted by 7—8 m $\mu$ , an effect also observed in (V).

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dimethyl fumarate,<sup>13</sup> on the ozonolysis of the tetraester of (V) to the photodimer (IX) of monomethyl fumarate,<sup>14</sup> on the formation of a five-membered cyclic anhydride on treatment with carbodi-imide, and on its spectroscopic data.

Two dimers of monomethyl trans, trans-muconate could be identified by thin-layer chromatography; after treatment with diazomethane they were both converted into the tetraester (VII) of the dimer (V) of trans, trans-muconic acid. (X), (XIII), and (XIV) remain as possible structures for the two dimers; one of them could be obtained pure by chromatography, and its structure established as (X) by cyclisation to the five-membered acid anhydride. The other dimer was very heat-labile, and underwent the Cope rearrangement at room temperature.\* Its structure could therefore be (XIII) or (XIV); we prefer the former, since (XIII), but not (XIV), can result from the dimerisation of parallel molecules in a 4 Å cell.

Polymers.—The polymeric materials obtained from (I) and (II) have molecular weights in the neighbourhood of



FIGURE 2 Absorption spectra of solid films of (A) monomethyl and (B) dimethyl trans, trans-muconate

7000—10,000, as determined by the ultracentrifugal method.<sup>10</sup> According to their ultraviolet and infrared spectra, some of the residual double bonds are not conjugated to the acid function; we may assume that some steps in the polymerisation process have taken place by 1,4-addition,

### DISCUSSION

The crystal structures of (I), (II), and (III) [Table; Figures 3, (4,5),<sup>5</sup> and 4] may be visualised as built of stacks, along a short axis, of parallel hydrogen-bonded molecules, the number of stacks and their contact geometry being determined by the symmetry elements and the dimensions of the unit cells. The packing arrangement of the diester (IV) (Figure 5) does not belong to the  $\beta$ -type, and it does not provide short centre-to-centre distances of antiparallel >C=C< groups, characteristic of the  $\alpha$ -type and leading to centrosymmetric dimers. We also note that the crystal structures



FIGURE 3 trans, trans-Muconic acid; packing arrangement projected on (001) 4



FIGURE 4 cis, cis-Muconic acid; packing arrangement seen along [001] <sup>6</sup>



FIGURE 5 Dimethyl trans, trans-muconate; packing diagram viewed normal to the molecular plane; only molecules related by the b- and c-axes are shown; molecules centred at (000), (001), (010), (011), (010), and (011);  $(1 \cdots 4')$  contact 3.7 Å

of (I), (II), and (IV) contain interstack contacts of approximately 3.7 Å between terminal carbons  $(1 \cdots 4')$  of the butadiene systems, and that these short contacts are absent in the *cis*-acid.

<sup>\*</sup> The cyclo-octadiene derivatives derived from (V) and (XI) have been characterised by their i.r., u.v., n.m.r., and mass spectra. The rates of the Cope rearrangements of the various dimers will be reported later.

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underlined by the absence of isomers such as (XVIII), in which the positions of the ring substituents are not compatible with the stereochemistry of the monomer. Their formation in the butadiene series has been interpreted in terms of a two-step mechanism <sup>26</sup> in which ringclosure of the diradical (XVII) is delayed sufficiently to permit rotation about the single bond and hence formation of (XIX) as well as of (XVIII). The stereospecific dimerisation in the solid-state reaction need not be interpreted as evidence against such a two-step mechanism; rather, we view it as one more piece of evidence for the postulate of minimum molecular motion in solidstate reactions.



We also draw attention to the strong support for the theoretical treatment  $^{27}$  of photochemical dimerisations provided by the relationship between monomer packing arrangement and the structures of the cyclodimers of (I), (II), and (III); the satisfactory correlation between theory and experiment demonstrates *inter alia* the power of crystallographic methods in the mechanistic analysis of nearest-neighbour reactions.

Two last points may be noted. First, the diester (IV) is stable at 25° to  $\lambda > 290$  mµ. Secondly, always under the same experimental conditions, oligomers could be obtained only from (I) and (II), but not from (III). It would be tempting to interpret the light-stability of dimethyl trans, trans-muconate in topochemical terms by asserting that the short  $(1 \cdots 4')$  contacts of 3.7 Å are inadequate for the formation of diradicals because of insufficient  $\pi$ -orbital overlap of nearest-neighbour double bonds in interstack, as compared with intrastack, contacts. The discussion of such a hypothesis, however attractive, must be postponed until we have considered in detail the topochemical effect on solidstate polymerisation, and can rule out the inhibition of the propagation reaction by the crystal structure under the conditions of temperature and crystal texture of our experiments. The absence of an isolable reaction product does not constitute proof of the impossibility of chemical interaction across the short  $(1 \cdot \cdot \cdot 4')$ contacts; the open-chain diradical to be expected from this interaction may not be able to propagate under the

Compounds (I), (II), and (III), which crystallise in the  $\beta$ -packing type, give divinyl-substituted cyclobutanes of molecular symmetry m, in which the stereochemistry of the monomers has been preserved. This retention of configuration is particularly striking in the instance of (III) whose photoreaction to the overcrowded dimer (XI) is not accompanied by isomerisation. (III) thus differs from the cis-acids in the cinnamic acid series crystallising in the  $\beta\text{-type}$  (Part IV  $^{22})$  which are rearranged to their trans-isomers instead of yielding the all-cis-substituted cyclobutane. Further evidence for lattice control over the photodimerisation of muconic acid derivatives is the formation of at least two cyclobutanes in a (sensitised) reaction, in solution,23 and the absence of a cyclobutane from solid dimethyl trans, trans-muconate. The argument is further strengthened by our observation <sup>24</sup> that the next higher homologue of (IV), dimethyl all-trans-hexatrienoate (XV), reacts in the solid phase to give the cyclodimer (XVI).



Two further points may be noted concerning cyclodimerisation. We have observed neither cyclohexenes nor cyclo-octadienes amongst the photoproducts. The former, which have been isolated  $^{25}$  in the sensitised solution reaction of buta-1,3-dienes, arise from interaction of the excited *cis*oid species with a ground-state molecule; since, in the solid state, all molecules have the *trans*oid conformation, the absence of cyclohexenes in our systems is understandable. The implied constraint of the matrix on the reaction path is further

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specific conditions of reaction employed so far. In particular the known steep temperature-dependence of propagation (as, *e.g.*, in the polymerisation of solid acrylic acid<sup>28</sup>) may be responsible for the inability of (IV) to polymerise. The formation of the oligomers from (I) and (II), but not from (III), does not settle the problem of reaction across short  $(1 \cdots 4')$  contacts, since we cannot decide at this stage whether the diradical (XVII) formed in the first step of the dimerisation process is also the one responsible for oligomer formation. If we assume this to be the case, the presence of short interstack contacts in (I) and (II), but not in (III), may provide a reaction path for propagation which is absent in (III). On the other hand, we may also have to envisage bond formation within a stack to a diradical which cannot be deactivated by cyclisation and which either reverts to monomer or else propagates. Further information in these various possibilities must await the results of present e.s.r. studies.

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