The Heterogeneous Thermal Transformation of the Yellow to the Orange Crystalline Form of Diethyl 2,5-Diaminoterephthalate. *X*-Ray Crystal Structures of the Two Forms [1,2]

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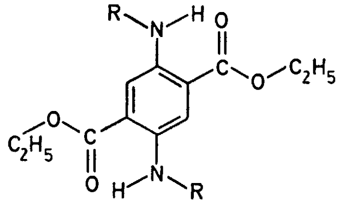
The structures of the yellow and orange forms of diethyl 2,5-diaminoterephthalate (1-Y) and (1-O) were determined by *X*-ray crystallography and the rearrangement of single crystals of (1-Y) to (1-O) studied. The structural results show that the reaction involves major changes in hydrogen bonding and also significant molecular reorientation. The reaction is shown by microscopic studies to be heterogeneous with nucleation at one or more sites followed by spread of a reaction front through the crystal. The nucleation process is difficult to influence. Yellow crystals of (1-Y) are monoclinic, $a = 7.937(2)$, $b = 12.721(4)$, $c = 7.022(3)$ Å, $\beta = 118.46(2)°$; the space group is $P2_1/c$ and the structure has been refined to R 0.043 on 989 non-zero reflections. There is a two-dimensional hydrogen-bonded net. Orange crystals of (1-O) are trigonal, $a = b = 21.859(8)$, $c = 6.937(3)$ Å; the space group is $R\bar{3}$ and the structure has been refined to R 0.077 on 3 063 non-zero reflections. In both forms, the molecules lie on crystallographic centres of symmetry. The three independently oriented molecules are nearly mutually orthogonal and there is a complex three-dimensional hydrogen bonding structure.

THERMAL solid state intramolecular transformations of organic compounds [3,4] have involved changes in molecular structure ranging in degree from no change at all (as in phase transformations such as the interconversion of α- and β-dichlorobenzene) [4] to reactions involving major intramolecular changes in both molecular bonding and molecular shape (as in the conversion of phenylazotribenzoylmethane into diphenyl triketone benzoylphenylhydrazone).[5] It has been profitable to categorize such solid state transformations in terms of two idealized mechanisms which have been designated as ' homogeneous ' and ' heterogeneous '.[2]

The homogeneous mechanism, which can be considered as a solid state counterpart of a solution reaction, proceeds by gradual replacement of starting molecules by product molecules at random sites throughout the crystal; the reaction must proceed through a continuous series of solid solutions as a crystal is transformed from starting material to product. There are fewer truly homogeneous reactions than superficial observation would suggest; a solid state change may seem to be of this type but on further investigation prove to be more complicated.[6,†]

The heterogeneous mechanism involves initiation at one or more nucleation sites followed by progression of reaction fronts throughout the crystal. Examples have included a transformation in which a hydrogen bonded chelate ring is opened during the change [9a] and one involving intramolecular rotation of six-membered rings.[9b]

Certain 3,5-diaminoterephthalic acid esters and their *NN'*-diaryl derivatives had been reported by Liebermann [10] to exist in polymorphic crystalline forms and to undergo thermal transformations from one to the other on heating. It was of interest to examine the crystallography of some of these compounds in order to broaden our understanding of the mechanisms by which such solid state transformations take place. This paper reports a study of the interconversion and structures determined by *X*-ray crystallography of the yellow and orange forms of the parent compound, diethyl 2,5-diaminoterephthalate (1-Y) and (1-O), and the following paper [11] reports on the pair of polymorphs of the *NN*-diphenyl derivative [(2-O) and (2-R)].



(1) R = H

(2) R = C_6H_5

EXPERIMENTAL

Spectra and other supplementary experimental data are available in ref. 1.

Synthesis.—Diethyl 2,5-diaminoterephthalate (1) was synthesized from diethyl 2,5-diaminodihydroterephthalate by dehydration with Pd–carbon in refluxing xylene [12] (with N_2 purging to remove the evolved hydrogen). Recrystallization from ethyl acetate gave a mixture of yellow (1-Y) and orange (1-O) crystals, m.p. 166—168 °C (lit.,[10] 167—168 °C); $\delta(CHCl_3)$ 1.4 (3 H, t), 4.35 (2 H, q), 5.0 (2.3 H, s), and 7.3 (2 H, s). Both forms gave identical spectra. C, H, and N analyses agreed with the theoretical values to within 0.3%. T.l.c. on silica gel (Eastman Chromagram Sheets 13181) using a variety of solvents showed a single spot for (1-Y), (1-O) obtained by crystallization, or (1-O) obtained by heating (1-Y), with the same R_F value in each case.

Differential scanning calorimetry (d.s.c.) employing a

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† Thermal reactions have also been observed to have only partial retention of crystallographic order.[7] The best studied examples of homogeneous reactions are photochemical rather than thermal.[8] An extensive study of the thermal rearrangements of substituted dibenzoyl peroxides has been made.[7] The extent of preservation of order has been measured and the geometric relationship of the product crystal axes to those of the starting crystal determined.

DuPont 900 thermal analyser equipped with a d.s.c. cell of (1-Y) and (1-O) showed the melting endotherm with an extrapolated onset of 172 °C. At heating rates of 5 or 10 °C min^{-1} (1-Y) and (1-O) showed the same behaviour with no evidence of a thermal change corresponding to the rearrangement of (1-Y). At 20 °C min^{-1} (1-Y) showed a small broad non-reproducible endotherm between 100 and 130 °C in some experiments. Samples of (1-Y) and (1-O) which were melted, cooled, and reheated showed only the melting endotherm described above.

Crystal Morphology of (1-Y).—The crystals were plates on (010): interfacial angles (°) calc., found (010):(100) 90, 89; (010):(001) 90, 89; (010):(110) 61.3, 61; (010):(111) 73.3, 73.*

Thermal Rearrangement of (1-Y) *to* (1-O).—Crystals of (1-Y) were separated from a mixture of (1-Y) and (1-O) obtained by crystallization of (1) from ethyl acetate or ethanol. The orange form predominated but the fraction of the yellow form could be increased by rapid cooling of a concentrated solution. Stored at ambient temperatures, both (1-Y) and (1-O) are stable for at least seven months.

Crystals of (1-Y) heated on a Mettler hot stage at a rate of 2—3 °C min^{-1} generally became orange between 70 and 125 °C with no sign of melting (melting occurred after the transformation at 164—166°). Crystals were photographed using a Bausch and Lomb polarizing microscope equipped with a Beseler Topcon Super D35 camera (exposure times 1 s with the crystal in the transmission position between crossed polarizing filters and 1—5 s with the crystal in the extinction position) (see Figure 1). The orange product 'crystal' was microcrystalline; when mounted on an *X*-ray powder camera without grinding, it gave 'arcs' which corresponded to those of (1-O) which had been obtained by crystallization and subsequently ground. However, the powder photograph of the rearrangement product showed a blotchy appearance indicative of some net orientation.

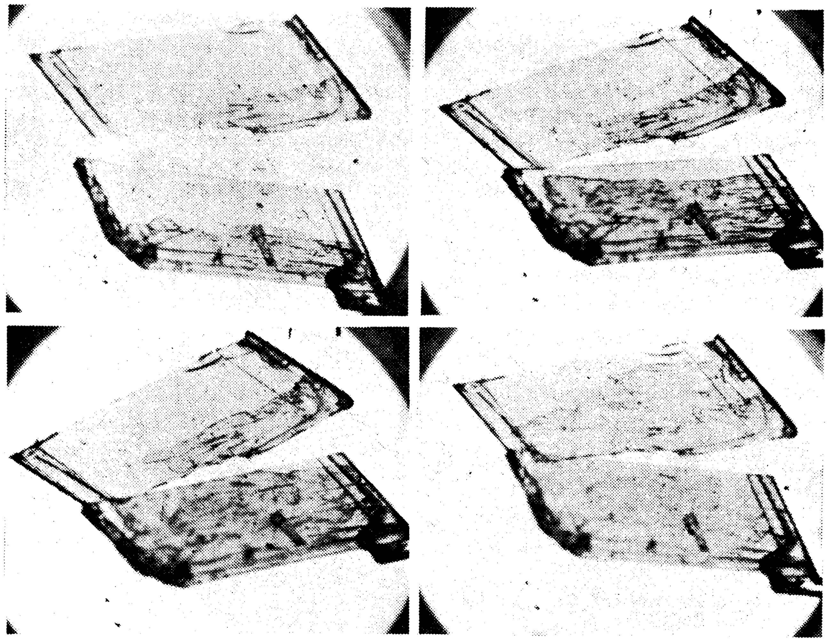

FIGURE 1 Rearrangement of two fragments of a yellow crystal of (1-Y) which had been broken through the middle. The crystals are being photographed with light from beneath the crystal. Upper left: the two halves at *t* 0. Note that the top half-crystal had been accidently rotated approximately 180° after the original crystal was fractured. Even at this time rearrangement had begun to occur, not at the fracture surfaces but in the opposite corner of one half and on the lower edge of the other. The orange disordered regions where rearrangement has occurred appear darker in these black-and-white photographs. Upper right: after 25 min at 45 °C the top half-crystal has not reacted much further but the bottom half-crystal shows that a reaction front approximately parallel to the long direction has progressed about three-quarters of the distance across it. Lower left: after 44 min at 45 °C the bottom half-crystal has reacted completely and the reaction of the top half-crystal is *ca.* 20% completed. Bottom right: after 81 min at 45 °C reaction of the upper half-crystal is *ca.* 75% completed. After additional heating for 120 min both half-crystals had undergone complete reaction

The temperature at which the reaction nucleated at one or more sites and the position of these sites were quite unpredictable. Most crystals reacted at temperatures between 75 and 125 °C and frontal migration was completed in 3—10 s. Two crystals were found to undergo nucleation at room temperature; at 45 °C the frontal migration was completed in *ca.* 15.5 h. The high speed and irregular pattern of frontal migration make it impossible to draw quantitative information from our data but a positive correlation between reaction temperature and time is at least hinted at by the following temperatures (°C) and reaction times (s) observed with six different crystals: 40, 4 000; 40, 7 000; 65, 2 000; 70, 120; 86, 25; 90, 90.

Attempts to influence the nucleation process were unsuccessful. Methods attempted were as follows: (1) prolonged heating at moderate temperatures (50—70 °C); (2) pricking with a pin; (3) cutting the crystal (although nucleation showed a preference for a crystal edge it reacted as often at a face formed by crystal growth as at a surface formed by cutting); (4) dipping crystals into liquid nitrogen; (5) placing microcrystals of toluene-*p*-sulphonic acid in contact

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* These values agree with those given by Groth (ref. 13) if the *c* axis therein is halved to agree with the *X*-ray value; thus the matrix to transform the axes given by ref. 13 to those in this paper is [1,0,0/0,1,0/0,0,1/2].

with various faces of crystals of (1-Y); (6) dipping into concentrated aqueous HCl; (7) exposure to u.v.; (8) fusing crystals of (1-Y) with (1-O).

X-*Ray Structure Determination of Yellow Diethyl* 2,5-*Diaminoterephthalate* (1-Y).—A crystal, *ca.* 0.8 × 0.5 × 0.4 mm, grown by recrystallization from ethyl acetate was suitable for *X*-ray work.

Crystal data.—$C_{12}H_{16}N_2O_4$, *M* 252.3, monoclinic, $a = 7.937(2)$, $b = 12.721(4)$, $c = 7.022(3)$ Å, $\beta = 118.46(2)°$, $U = 623.3$ Å^3; $Z = 2$, $D_c = 1.34$ g cm^{-3}; μ(Cu-K_α) = 8.6 cm^{-1}; $F(000) = 268$; systematic absences, $h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$; space group $P2_1/c$. Unit cell parameters were determined by a least squares fit to the settings for fifteen accurately centred high-order reflections (Cu-K_α, $\lambda = 1.541\,78$ Å). Intensity data were collected on a computer-controlled four-circle Syntex $P2_1$ diffractometer. Procedures for data collection have been described previously.[14] A total of 989 reflections was considered non-zero at the 1.96σ significance level out of 1 046 possible reflections in the 2θ range 2—130°. No absorption or extinction corrections were applied and there was no evidence for crystal decomposition. The weights were taken as $1/[\sigma(F_o)^2 + (0.02F_o)^2]$, where $\sigma(F_o)$ is the standard deviation based on counting statistics. The scattering factors were taken from the analytical expressions given in ref. 15.

TABLE 1

Final atomic parameters for (1-Y) in fractions of the unit cell edge[a]

Atom	*X*	*Y*	*Z*
O(1)	0.828 2(2)	0.403 16(9)	0.299 3(3)
O(2)	0.736 7(2)	0.567 52(9)	0.187 5(2)
N(1)	0.669 4(2)	0.303 45(11)	0.514 5(3)
C(1)	0.476 4(2)	0.415 98(11)	0.607 7(2)
C(2)	0.591 3(2)	0.402 08(10)	0.510 1(2)
C(3)	0.615 0(2)	0.489 03(11)	0.400 1(2)
C(4)	0.735 9(2)	0.480 49(12)	0.292 9(2)
C(5)	0.858 1(3)	0.565 25(15)	0.085 1(3)
C(6)	0.847 2(3)	0.669 67(16)	−0.016 0(3)
NH(1)	0.685(3)	0.256(1)	0.626(3)
NH(2)	0.761(3)	0.300(2)	0.473(3)
H(1)	0.458(2)	0.359(1)	0.687(2)
H(2)	0.983(3)	0.553(2)	0.187(4)
H(3)	0.814(3)	0.505(2)	−0.016(3)
H(4)	0.916(3)	0.671(2)	−0.097(3)
H(5)	0.703(4)	0.684(2)	−0.123(4)
H(6)	0.896(3)	0.727(2)	0.092(3)

[a] The rest of the molecule is generated by the centre of symmetry at ½,½,½.

The structure was solved using the MULTAN program.[16] Least squares refinement incorporating positional and anisotropic temperature parameters for the non-hydrogen atoms gave *R* 0.09. An electron density difference map revealed the positions of four of the eight hydrogen atoms; the remaining positions were calculated assuming standard bond lengths and angles. Refinement incorporating positional and anisotropic thermal parameters for the non-hydrogen atoms with positional and isotropic temperature factors for the hydrogen atoms gave a final *R* of 0.043 and an R_2 of 0.075.[*] The 'goodness of fit' between the calculated and observed models was 2.49. The final electron density difference map did not reveal any significant electron density above 0.14 e Å^{-3}.

The final atomic co-ordinates for (1-Y) are listed in Table 1. The values of the thermal parameters and of the structure factors are in Supplementary Publication No. SUP 23148 (14 pp.)[†]

X-*Ray Structure Determination of Orange Diethyl* 2,5-*Diaminoterephthalate* (1-O).—A crystal approximately 0.5 × 0.4 × 0.2 mm cut from a large rod-like crystal grown by recrystallization from ethyl acetate was used for data collection.

Crystal data.—$C_{12}H_{16}N_2O_4$, *M* 252.3, trigonal, cell data (hexagonal axes) $a = b = 21.859(8)$, $c = 6.937(3)$ Å, $U = 2\,870.5$ Å^3, $Z = 9$, $D = 1.31$ g cm^{-3}, $F(000) = 1\,206$; systematic absences, $hkil$ when $-h + k + l = 3n$, $000l$ when $l = 3n$; space group $R3$ or $R\bar{3}$, the latter being confirmed by the results of the analysis. Cell data (trigonal axes) $a = 12.831$ Å, $\alpha = 116.83°$, $U = 956.4$ Å^3.

The procedures for the determination of cell parameters, data collection, and the weighting schemes and scattering curves used were as for (1-Y). A total of 3 063 reflections was considered non-zero at the 1.96σ significance level out of 3 544 possible reflections in the 2θ range 2—130°. There was no evidence for crystal decomposition.

The structure was solved using the MULTAN program.[16] Least squares refinement, initially in space group $R3$, incorporating positional and anisotropic temperature parameters for the non-hydrogen atoms gave *R* 0.099. An electron density difference map revealed the positions of four of the eight hydrogen atoms; further least squares refinement including positional parameters and isothermal temperature factors for the hydrogen atoms resulted in *R* 0.078. However, many of the molecular dimensions were unreasonable. As many chemically-equivalent dimensions were distributed roughly equally greater and less than the expected value, we took this as an indication that the molecule should be at a crystallographic centre of symmetry. Accordingly, $R\bar{3}$ was chosen as the space group. Further refinement in space group $R\bar{3}$ with the centre of symmetry of the molecule shifted to the special position (1/2,0,1/2), followed by an electron density difference map, revealed the

TABLE 2

Final atomic co-ordinates for (1-O) in fractions of the unit cell edge[a]

Atom	*X*	*Y*	*Z*
O(1)	0.448 53(5)	0.047 27(6)	0.965 12(15)
O(2)	0.563 91(5)	0.117 14(5)	0.907 04(15)
N(1)	0.368 46(7)	−0.036 57(8)	0.662 18(20)
C(1)	0.437 72(6)	−0.046 37(6)	0.410 34(19)
C(2)	0.433 54(6)	−0.018 05(6)	0.586 70(17)
C(3)	0.498 23(6)	0.029 96(6)	0.676 65(17)
C(4)	0.499 18(6)	0.063 89(6)	0.862 08(18)
C(5)	0.596 66(8)	0.154 19(9)	1.085 58(24)
C(6)	0.646 03(11)	0.208 10(14)	1.108 92(34)
NH(1)	0.334 2(10)	−0.061 0(9)	0.598 6(27)
NH(2)	0.369 4(11)	−0.017 2(11)	0.795 4(39)
H(1)	0.395 8(9)	−0.073 6(9)	0.350 8(26)
H(2)	0.549 1(12)	0.125 3(11)	1.191 2(35)
H(3)	0.546 7(11)	0.182 9(10)	1.070 7(30)
H(4)	0.648 4(11)	0.235 5(11)	1.226 6(35)
H(5)[b]	0.664 0(0)	0.240 0(0)	0.993 0(0)
H(6)	0.676 5(12)	0.185 0(13)	1.121 6(36)

[a] The rest of the molecule is generated by the centre of symmetry at ½,0,½. [b] The position of this atom was not varied.

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[*] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{\frac{1}{2}}$, m = number of observations, n = number of variables.

[†] For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index Issue.

positions for all the hydrogen atoms. Further full matrix least squares refinement incorporating positional parameters for all atoms, isotropic temperature factors for all hydrogen atoms and anisotropic temperature factors for non-hydrogen atoms gave a final R of 0.077 and R_2 of 0.123. The ' goodness of fit ' between the calculated and observed models was 1.4. A final electron density difference map did not reveal any significant electron density above 0.22 e Å^{-3}.

The final atomic co-ordinates for (1-O) are listed in Table 2. The values of the thermal parameters and of the structure factors are in SUP 23148.

RESULTS AND DISCUSSION

The yellow and orange forms (1-Y) and (1-O) were obtained together on recrystallization of (1) from common solvents and were hand separated. In agreement with the work of Liebermann, (1-Y) generally rearranged to (1-O) when heated to temperatures between 70 and 125 °C, more than 40 °C below the melting point of (1-O); since (1-Y) always rearranged before it melted it was not possible to measure its m.p. Examination of the behaviour of single crystals (see Figure 1) showed the reaction to be a heterogeneous one; reaction began at one or more nucleation sites (often only one)* and the front(s) which had been formed then spread throughout the crystal. Although initiation of reaction often took hours of heating at the low end of the temperature range (or rapid heating to the higher end) the time required for frontal migration was generally only a few seconds. The change of (1-Y) to (1-O) was found to occur even at room temperature; it follows therefore that (1-O) is the stable form over the entire temperature range we have employed (25—125 °C). Microscopic examination of the crystal between crossed polarizing filters showed that regions of the crystal ahead of the front still extinguished normally whereas regions remaining after its passage no longer extinguished. Although the overall shape of the crystal was maintained, the top surface became rough and in some cases tiny cracks appeared after reaction. The reaction front was a sharp border between the yellow and orange phases and appeared to extend from the top to the bottom and to be nearly parallel to the side faces of the crystal. There was otherwise no clear relationship between the direction of migration of the front and the internal structure of the crystal. The product ' crystal ' was shown by *X*-ray powder photography to be an aggregate of microcrystallites of (1-O).

Determination of the structures of (1-Y) and (1-O) by *X*-ray crystallography revealed the nature of the change required for the transformation. In Figure 2 are shown the structures of the molecules of the two forms. (The *X*-ray results will be discussed in more detail later.) The molecules of (1) in both (1-Y) and (1-O) lie on crystallographic centres of symmetry and are nearly planar. In each case there is an internal hydrogen bond between one of the amine hydrogen atoms and the adjacent

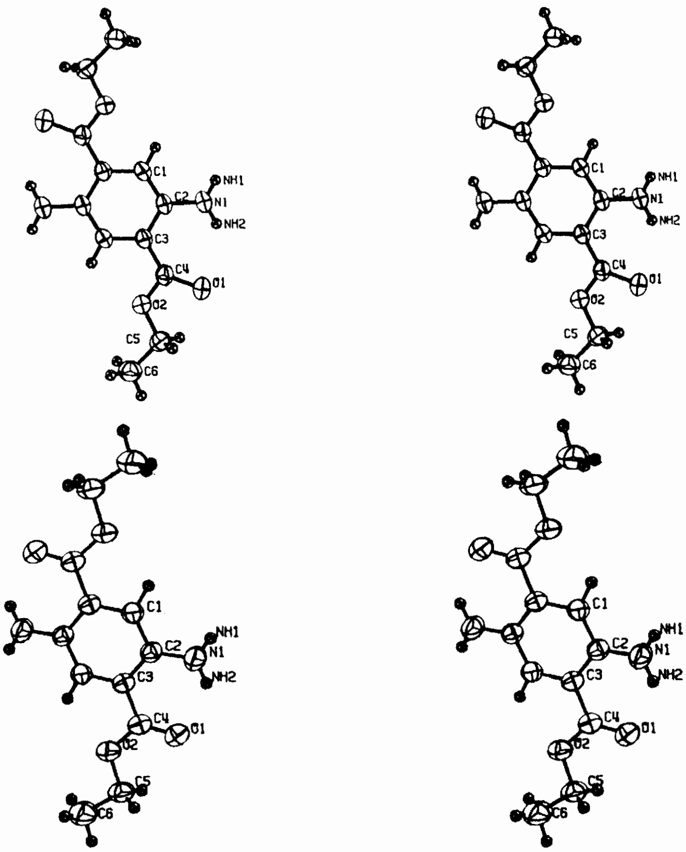

FIGURE 2 Stereoscopic view of the molecules of (1) in the two forms. (*a*) Form (1-Y). (*b*) Form (1-O). Both molecules lie on crystallographic centres of symmetry

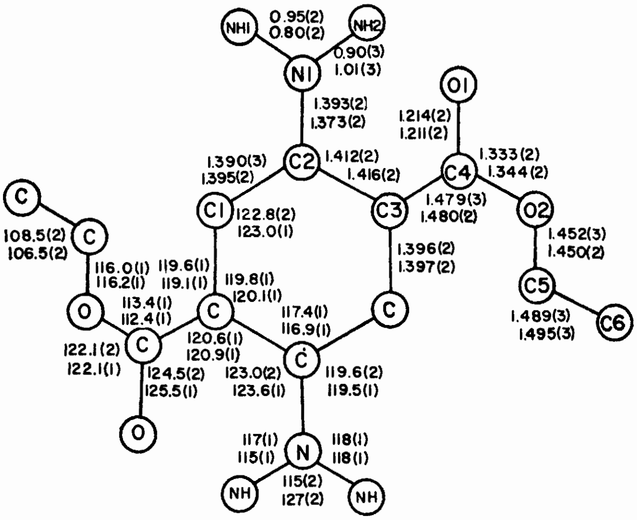

FIGURE 3 Bond lengths (Å) and angles (°) in the two forms (1-Y) and (1-O) of diethyl 2,5-diaminoterephthalate. The values for (1–Y) are given above those for (1-O)

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* It should be noted that the number of nucleation processes observed during the reaction of a single crystal is related to the average time between nucleations, t_n (1/frequency of nucleation) and to the time t_f required for a reaction front to move completely through the crystal once nucleation has occurred. If $t_n \gg t_f$ each crystal will react by a single nucleation process whereas if $t_n \ll t_f$ there will be so many nucleation processes with the formation of a correspondingly large number of independent reaction fronts that the possibility of deducing by visual inspection that reaction is cleanly heterogeneous will have been lost.

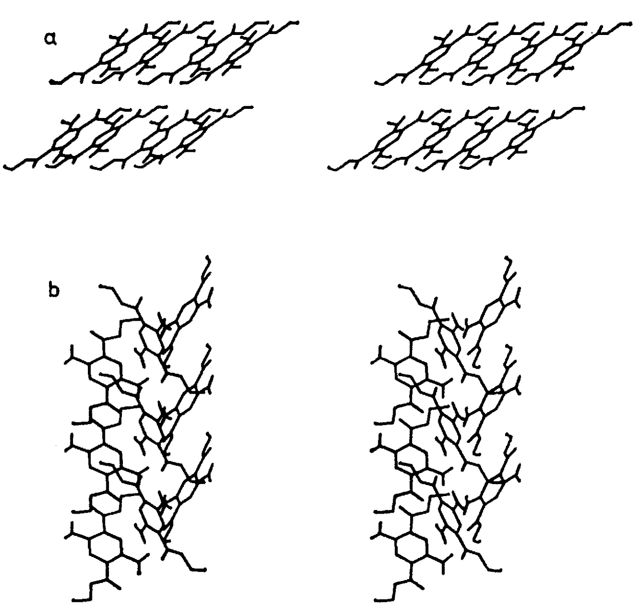

FIGURE 4 (*a*) Stereopair drawing of the structure of the yellow form (1-Y) of diethyl diaminoterephthalate. The orientation is the same as that in the photographs (Figure 1) of crystals rearranging. The *b* axis is into the page, *c* is to the right and *a* is toward the bottom of the page and to the left. Note the antiparallel carbonyl interaction between pairs of molecules related by translation along *a*. (*b*) Stereopair drawing of the orange form (1-O) of the same compound showing a column of molecules related by the 3_1 axis. This is a view along [110]. The *c* axis is vertical in the plane of the page and *a* and *b* are coming out from the page 60° to either side of the normal. Again note the antiparallel arrangement of carbonyl groups of molecules related by translation along *c*

carbonyl oxygen atom. The most striking difference between the molcules in the two crystals is that in (1-Y) the amine groups appear pyramidal and the lengths of the bonds (Figure 3) between the amine nitrogen atoms and the adjacent carbons of the aromatic rings is 1.393(2) Å whereas in (1-O) the amine hydrogen atoms lie in the plane of the benzene ring and the corresponding N–C lengths are 1.373(2) Å. This suggests an increased resonance interaction of the amine groups in (1-O) with the aromatic ring. However, the ester groups in the two structures show bond lengths which are not distinguishable on the basis of the present analysis. A further difference between the two structures is that the best plane through the essentially planar carbonyl groups makes an angle of only 3.3° with the plane of the aromatic ring in (1-Y) but an angle of 11.4° with the ring in (1-O). The difference in colour of the two crystal forms may be related to the difference in amine geometry but more information is needed before the rather subtle difference between the two structures can be fully interpreted. In any case it is clear that the change in molecular structure required to transform (1-Y) to (1-O) is very minor and would have little or no activation energy were the molecules in an isolated state.

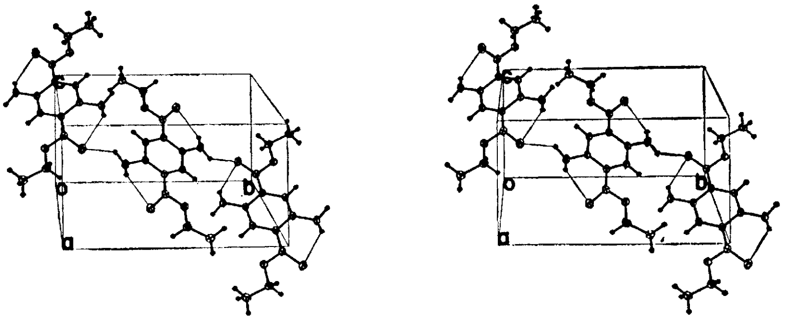

FIGURE 5 Stereoscopic view of the packing of the molecules in the (1-Y) crystal. The reference molecule is in the centre of the cell with the asymmetric unit related to the other half by the centre at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

The question of whether a change of this type should be classified as a ' reaction ' or a ' phase transition ' is a subtle one.[3a,9] Although there is a change in molecular structure which can be described in terms of isolated molecules (the criterion which has been proposed for a ' reaction ') it is minimal and clearly associated with the change in crystal environment.

Even though the change in molecular structure in the course of the transformation of (1-Y) to (1-O) is relatively slight the change in crystal packing is very great. This can best be appreciated by inspection of Figure 4. In the starting crystal (1-Y) there are molecules with only two different orientations relative to the unit-cell directions, the angle between the planes of their benzene rings being only 34°; the remainder of the structure can be considered as being formed by simple translation of these two types of molecules (Figure 4a). In the structure of (1-O), on the other hand, there are molecules with three different orientations nearly mutually perpendicular to each other (the angle between the benzene rings of any two of these three molecules is 81°) (Figure 4b). A further difference in the two structures arises from differences in the intermolecular hydrogen bonding to be discussed later. Consequently there can be no subtle path for transition between (1-Y) and (1-O); instead it seems probable that there is a disordered region at the interface between the two forms from which the structure of (1-O) develops.

Figure 4a shows a view of the internal structure of (1-Y) in the orientation of the crystals of Figure 1. Development of the front might be expected to be highly anisotropic with respect to the directions parallel to the

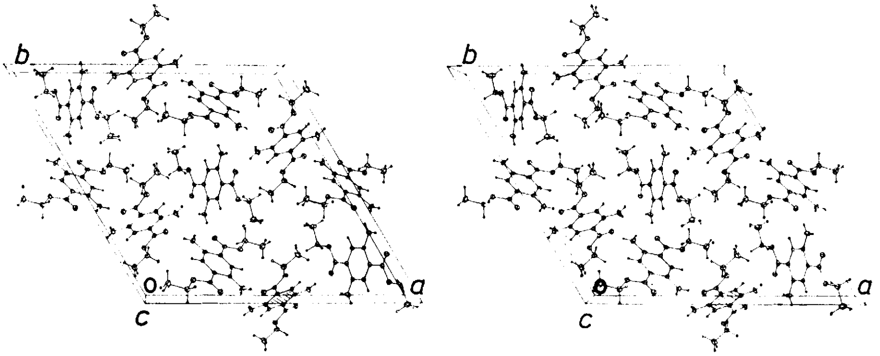

FIGURE 6 Stereoscopic view of the packing of molecules of (1-O) in the crystal. The phenyl ring of the reference molecule is shaded. The cavity shown to the upper left of the cell is more apparent than real as parts of the molecules (which are not shown) in adjacent unit cells in the *c* direction do intrude into that space

major crystal face as had been observed in a previous case.[9a] However, although there was a pronounced tendency for the front to be parallel to the side crystal faces, there was no simple correlation of a preferred direction of formation with crystal structure.

X-Ray Crystal Structures and Molecular Packing of (1-Y) *and* (1-O).—The structure of (1-Y) in space group $P2_1/c$ with two centrosymmetric molecules per unit cell has as its most interesting structural features the hydrogen bonding, both intramolecular and between neighbours related by the screw axis along *b* and by the glide plane operation along *c* (Figure 5), and an interaction between antiparallel carbonyl groups * of adjacent molecules (Figure 4a).

The structure of (1-O) is unusual in that it is trigonal in space group $R\bar{3}$, a space group relatively rare among organic crystals.[20] With nine molecules per unit cell the molecule is again centrosymmetric as in (1-Y). Each molecule is hydrogen bonded internally and to each of six neighbours so that the crystal is held together by hydrogen bonding in every direction (Figure 6). The resultant structure is slightly less dense than the structure of (1-Y) with a molecular volume of 319 Å^3 as compared with 312 Å^3.

Conclusions.—This transformation together with the other solid state reactions studied suggests that the heterogeneous mechanism may be generally found in the thermal reactions of crystals of intermediate molecular size whose change in molecular structure could be expected to occur very rapidly in solution at the reaction temperature. The extent of change of molecular shape and degree of redirection of hydrogen bonding required seem to be secondary factors in determining the type of mechanism.

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* The distance between C(4) (x,y,z) and O(1) ($2-x$, $1-y$, $1-z$) is 3.59 Å, a distance longer than that observed in 4-t-butylcyclohexanone (3.12 Å)[17] or cyclohexa-1,4-dienone (3.13 Å).[18] However the dipole–dipole forces between antiparallel carbonyl groups 3.6 Å apart in ethyl 4-(4-methoxybenzylideneamino)cinnamate were calculated to contribute a stabilization energy of as much as 7.9 kcal mol^{-1}.[19]

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