The Heterogeneous Thermal Transformation of the Orange Diethyl *NN'*-Diphenyl-2,5-diaminoterephthalate Benzene Complex to the Red Solvent-free Compound. *X*-Ray Crystal Structures of the Two Forms [1,2]

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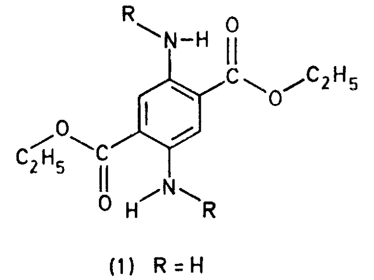
The orange form of diethyl *NN'*-diphenyl-2,5-diaminoterephthalate (2) which had been reported by Liebermann has been found, when formed by recrystallization from benzene, to be a benzene complex (2)–benzene (1 : 1). The ready transformation of benzene complex (2-O) to the red benzene-free compound (2-R) has been studied. Reaction of single crystals proceeds by nucleation followed by frontal migration leading first to a metastable, partially disordered, yellow phase and a second front leading to the red product (2-R). The reaction is very readily affected by mechanical stress and also by the presence of the vapour of ethanol, acetone, or even water, in contrast to the transformation of diethyl 2,5-diaminoterephthalate (1-Y) discussed in the previous paper. The crystal structures of (2-O) and (2-R) were determined by *X*-ray methods. An orange crystal of the benzene complex of (2-O), immersed in benzene mother liquor in a capillary tube, was monoclinic, $a = 15.355(5)$, $b = 7.863(2)$, $c = 22.303(7)$ Å, $\beta = 100.18(3)°$; the space group is $P2_1/c$ with four molecules in the unit cell and the structure has been refined to an *R* factor of 0.055 on 2 858 non-zero reflections. The structure is composed of pairs of crystallographically independent, but centrosymmetric, molecules of (2) related to each other by a near two-fold rotation axis. The benzene molecules are ordered and situated in channels with periodic constrictions. Red crystals of (2-R) are triclinic, $a = 10.124(5)$, $b = 4.025(1)$, $c = 13.623(8)$ Å, $\alpha = 90.46(4)°$, $\beta = 106.95(4)°$, $\gamma = 99.63(4)°$; the space group was $P\bar{1}$ with one molecule in the unit cell and the structure was refined to an *R* factor of 0.043 on 1 496 non-zero reflections. The structure is formed by translation in three dimensions of the crystallographically centrosymmetric molecule.

A SERIES of derivatives of diethyl 2,5-diaminoterephthalate had been shown by Liebermann [3] to exist in dual crystalline forms, the two forms differing in colour. In the preceding paper [4] the *X*-ray crystal structures of the yellow and orange forms (1-Y) and (1-O) of the parent compound were reported together with a study of the thermal conversion of the yellow into the orange form in the solid state.



(1) R = H

(2) R = C_6H_5

Liebermann had reported that the *NN'*-diphenyl derivative of (1) existed in orange and red forms.[3] In the present paper we report on the structures of these compounds and on the spontaneous conversion of (2-O) † into (2-R) and the reverse process; at the outset of our investigation it was found that our orange modification was in fact a benzene solvate of (2) and the study of the interconversion of (2-O) and (2-R) has had, as an additional feature of interest, the loss or incorporation of benzene from the crystal.

EXPERIMENTAL

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

Synthesis.—Diethyl *NN'*-diphenyl-2,5-diaminoterephthalate [(2-O) and (2-R)] were synthesized from diethyl 2,4-diaminodihydroterephthalate by treatment with aniline and air. Recrystallization from ethanol of the product first obtained gave tiny red needles of (2-R), m.p. **144—146** °C; $\nu_{max.}$ (KBr disc) 3 375, 3 000, 1 705, and 1 608 cm^{-1}; $\nu_{max.}$ ($CHCl_3$) 3 360, 3 020, 1 685, and 1 595 cm^{-1}; δ ($CHCl_3$) 1.3 (3 H, t), 4.3 (2 H, q), 7.1 (7.7 H, m), 8.0 (1 H, s), and 8.7 (1 H, s). Carbon, hydrogen, and nitrogen analyses agreed with the calculated values to within 0.3%.

Recrystallization from a variety of solvents (methanol, ethanol, acetonitrile, glacial acetic acid, ethyl acetate, chloroform, acetone, toluene, carbon tetrachloride) gave tiny red needles. However, orange powders were obtained by rapid recrystallization from pyridine, benzene, cyclohexane, carbon tetrachloride, methanol, acetone, or methylene dichloride at the temperature of a dry ice–acetone bath. These orange powders were very unstable; when collected by removing the solvent at acetone–dry ice temperatures they turned red as soon as they were taken from the bath and allowed to warm. The m.p.s and i.r. and n.m.r. spectra were identical with those of (2-R) described above; however, the crystals had turned red during the i.r. (KBr disc) measurement by the time the measurement had been completed.

Large orange crystals of (2-O) were obtained by slow

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† In refs. 1 and 2, the yellow-orange compound (2-O) has been referred to as orange and yellow, respectively.

evaporation of a benzene solution at room temperature. These were stable below 0 °C or when kept in an atmosphere saturated with benzene vapour. Otherwise they gradually turned red under ambient conditions. During the m.p. determination they turned red very quickly on heating and showed m.p. 144—146 °C. An elemental analysis could be obtained in reasonable agreement with that expected for a 1 : 1 complex of (2) with benzene (Found: C, 74.3; H, 6.6; N, 6.2. Calc. for $C_{24}H_{24}N_2O_4 \cdot C_6H_6$: C, 74.7; H, 6.3; N, 5.8. Calc. for $C_{24}H_{24}N_2O_4$: C, 71.0; H, 6.4; N, 6.9%). Other analysis suggested molar ratios of benzene : (2) of from less than 0.5 to 1.

Because of instability crystals of (2-O) were not submitted to goniometric measurements. Differential scanning calorimetric studies of (2-R) showed only a melting endotherm with an extrapolated onset of 145 °C. Isomer (2-O) gave a very uneven baseline followed by a melting endotherm which occurred between 142 and 146 °C.

Thermal Rearrangement of (2-O) *to* (2-R).—Loss of benzene from six samples of (2-O) crystals obtained from two different crystallizations was followed quantitatively. Crystals removed from the benzene mother liquor, dried by suction filtration, and weighed at regular intervals were allowed to stand under ambient conditions; the total weight loss was that expected for an initial 1 : 1 complex to be completely desolvated. Similar crystals observed on the stage of a polarizing microscope at the same time intervals appeared completely red when 30—70% of the benzene had been lost. Figure 1 shows the loss of benzene as a function of time.

Orange single crystals of (2-O), taken from a sample obtained by slow recrystallization from benzene and having a correct C, H, and N analysis, were stable below 0 °C or in an atmosphere saturated with benzene, though when kept below 0 °C for more than a few days they often had orange opaque areas. They developed red areas soon after being brought to ambient conditions and had become red in 1 h. No indication of melting or softening was observed during this process. Placed on the stage of a Bausch and Lomb polarizing microscope equipped with a Besseler Topcon Super D 35 mm camera, the crystals were observed and photographed at regular intervals with exposure times of 1 s with the crystal in the transmission position and 5 s in the extinction position. The surfaces of the freshly prepared crystals were smooth and there was good extinction when the crystal was rotated between crossed polarizing filters. After 5—10 min, areas of the crystal, usually along the edges and at visible defects, became opaque but remained orange. This change was most readily visible when the crystal was rotated between polarizing filters since these opaque areas no longer showed the usual extinction (see Figure 1). The opaque regions then spread throughout the crystal. Behind the opaque orange front a second red front developed (also opaque). The side faces of the crystal appeared to react in preference to the top and bottom faces and there were examples in which the reaction front was not uniform from the top to the bottom of the crystals but occurred in a thin horizontal section; in one crystal the top face had become red while side faces still remained orange. In some cases thin red areas extended over portions of the crystal which still showed extinction. The red product when photographed (without grinding) on an *X*-ray powder camera gave a typical powder photograph identical with that from ground (2-R).

Nucleation of the reaction could be readily effected by mechanical deformation such as pricking with a pin. The reaction was also accelerated by the presence of water vapour. Crystals which had been stored in a desiccator at 20 °C and warmed to room temperature in the desiccator to prevent condensation of water on the surface required 2 h for reaction in contrast with comparable crystals which required 1 h when no such precautions were taken. The presence of acetone or ethanol vapour accelerated reaction and washing (2-O) with liquid acetone or ethanol caused the crystal to become red immediately. It was noted that crystals which had less than the full 1 : 1 ratio of benzene (*i.e.* vacant benzene sites) reacted much faster than those with a 1 : 1 ratio.

The reaction could be reversed by placing fully or partially reacted crystals in a benzene atmosphere. After 5 h, a partially reacted crystal of (2-O) in a benzene-saturated atmosphere appeared totally orange when viewed by transmitted light. The portions of the crystal which had previously reacted now were opaque but no longer appeared red. The portions which had not reacted still showed extinction between crossed polarizing filters. No further change was noted as long as the crystal was maintained in the benzene saturated atmosphere. Another crystal of (2-O) had become completely red after 24 h at room temperature; when placed in a benzene atmosphere for 60 h it returned to orange but was still completely opaque when viewed by transmitted light.

X-*Ray Structure Determination of Orange Diethyl* NN′-*Diphenyl*-2,5-*diaminoterephthalate.—Benzene* 1 : 1 *Complex* (2-O).—Intensity data were collected with a fragment of (2-O) cut from a long flat needle grown by slow recrystallization from benzene, wedged inside a 0.5 mm capillary, and surrounded by mother liquor; the ends of the capillary were sealed first with quick-drying epoxy-cement and then with Krylon (crystal clear protective spray coating for electronic uses). The long crystal axis was *b*.

Crystal Data.—$C_{24}H_{24}N_2O_4 \cdot C_6H_6$, $M = 482.6$, monoclinic, $a = 15.355(5)$, $b = 7.863(2)$, $c = 22.303(7)$ Å, $\beta = 100.18(3)°$, $U = 2\,650.4$ Å^3, $Z = 4$, $D_c = 1.21$ g cm^{-3}; $F(000) = 1\,024$; 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, λ 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.[5] A total of 2 858 reflections was considered non-zero at the 1.96σ significance level out of 4 312 possible reflections in the 2θ range 2—127°. No absorption or extinction corrections were applied and there was no evidence for crystal decomposition. The weights were taken as $1/[\sigma(F_0)^2 + (0.02F_0)^2]$, where $\sigma(F_0)$ is the standard deviation based on counting statistics. The scattering factors were taken from the analytical expressions given in ref. 6.

The structure was solved using the MULTAN program.[7] Least squares refinement incorporating positional and anisotropic temperature parameters for the non-hydrogen atoms gave *R* 0.094. An electron density difference map revealed the positions of all hydrogen atoms including those for the benzene molecule. After two further cycles of refinement, the positional and thermal parameters for those hydrogen atoms which had large B_{iso} values were not varied further. Additional refinement incorporating positional parameters for all other atoms with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors

TABLE 1

Atomic co-ordinates for (2-O) in fractions of the unit cell [a,b]

Atom	*X*	*Y*	*Z*
O(1A)	0.067 2(1)	0.539 6(3)	0.167 94(8)
O(2A)	0.148 3(1)	0.341 9(3)	0.131 59(8)
N(1A)	−0.083 1(2)	0.633 2(3)	0.092 56(10)
C(1A)	−0.079 4(2)	0.583 5(4)	−0.014 53(11)
C(2A)	−0.042 6(2)	0.566 3(3)	0.046 78(11)
C(3A)	0.039 2(2)	0.480 5(3)	0.061 03(10)
C(4A)	0.084 7(2)	0.459 2(4)	0.125 14(12)
C(5A)	0.197 7(2)	0.317 9(5)	0.193 09(12)
C(6A)	0.275 1(3)	0.209 8(5)	0.188 82(17)
C(7A)	−0.171 7(2)	0.679 8(4)	0.090 00(11)
C(8A)	−0.241 8(2)	0.608 5(4)	0.050 42(13)
C(9A)	−0.327 6(2)	0.659 8(5)	0.051 62(15)
C(10A)	−0.345 1(2)	0.779 8(5)	0.092 59(17)
C(11A)	−0.276 3(2)	0.848 5(4)	0.132 86(16)
C(12A)	−0.190 3(2)	0.800 0(4)	0.131 57(13)
O(1B)	0.052 0(1)	−0.021 0(3)	0.169 16(8)
O(2B)	−0.052 6(1)	0.172 9(3)	0.138 28(7)
N(1B)	0.146 8(2)	−0.121 2(4)	0.082 80(11)
C(1B)	0.067 1(2)	−0.085 5(4)	−0.020 62(11)
C(2B)	0.074 3(2)	−0.059 7(4)	0.041 81(11)
C(3B)	0.004 8(2)	0.026 7(3)	0.062 33(10)
C(4B)	0.005 4(2)	0.055 2(4)	0.128 53(12)
C(5B)	−0.063 5(2)	0.201 8(4)	0.201 30(11)
C(6B)	−0.149 0(2)	0.290 5(5)	0.199 41(15)
C(7B)	0.229 0(2)	0.171 9(4)	0.070 46(12)
C(8B)	0.274 9(2)	−0.297 9(4)	0.106 30(15)
C(9B)	0.356 8(3)	−0.351 1(5)	0.096 04(19)
C(10B)	0.393 8(3)	−0.281 4(5)	0.050 07(20)
C(11B)	0.349 8(2)	−0.155 4(6)	0.015 20(18)
C(12B)	0.268 2(2)	−0.099 6(5)	0.025 04(15)
C(13)	0.493 2(3)	0.168 7(9)	0.117 54(24)
C(14)	0.546 7(4)	0.306 6(7)	0.121 42(24)
C(15)	0.601 6(3)	0.343 8(6)	0.173 59(29)
C(16)	0.603 0(4)	0.244 6(9)	0.222 79(25)
C(17)	0.549 5(5)	0.104 1(9)	0.219 81(28)
C(18)	0.493 6(4)	0.067 2(7)	0.165 79(36)
H(13) [c]	0.453(0)	0.144(0)	0.078 0(0)
H(14)	0.546(0)	0.382(0)	0.085 2(0)
H(15)	0.641(0)	0.445(0)	0.176 3(0)
H(16)	0.643(0)	0.272(0)	0.261 8(0)
H(17)	0.551(0)	0.028(0)	0.255 7(0)
H(18)	0.453(0)	−0.032(0)	0.162 1(0)
H(8A)	−0.231(0)	0.522(0)	0.024 6(0)
H(9A)	−0.375(0)	0.609(0)	0.021 2(0)
H(10A)	−0.403(0)	0.815(0)	0.095 5(0)
H(11A)	−0.287(0)	0.936(0)	0.159 4(0)
H(12A)	−0.142(0)	0.849(0)	0.160 4(0)
H(2A)	0.218(0)	0.432(0)	0.211 0(0)
H(3A)	0.160(0)	0.264(0)	0.219 4(0)
H(8B)	0.250(2)	−0.349(4)	0.138 0(14)
H(9B)	0.386(2)	−0.446(4)	0.117 6(15)
H(10B)	0.454(2)	−0.338(4)	0.040 2(16)
H(11B)	0.372(2)	−0.095(4)	−0.017 0(15)
H(12B)	0.241(2)	−0.004(4)	0.003 8(12)
H(1A)	−0.131(2)	0.644(4)	−0.026 9(12)
NH(1A)	−0.048(2)	0.643(3)	0.127 9(12)
H(4A)	0.256(0)	0.103(0)	0.166 3(0)
H(5A)	0.317(0)	0.272(0)	0.167 1(0)
H(6A)	0.307(0)	0.181(0)	0.233 4(0)
H(1B)	0.113(2)	−0.147(3)	−0.037 9(12)
NH(1B)	0.138(2)	−0.127(4)	0.117 4(13)
H(2B)	−0.014(0)	0.269(0)	0.219 1(0)
H(3B)	−0.062(0)	0.084(0)	0.220 3(0)
H(4B)	−0.157(0)	0.319(0)	0.235 9(0)
H(5B)	−0.200(0)	0.214(0)	0.177 4(0)
H(6B)	−0.156(0)	0.400(0)	0.176 8(0)

[a] Atoms are designated by A if they belong to one of the independent molecules and by B if they belong to the second one. C(13)—C(18) are the atoms of the benzene solvate. [b] The rest of molecule A can be generated by the centre of symmetry at 0, ½, 0. The rest of molecule B can be generated by the centre of symmetry at 0, 0, 0. [c] A standard deviation of zero indicates that this parameter was not varied in the refinement.

for the hydrogen atoms gave a final R * of 0.055 and an R_2 of 0.057 on the non-zero data. The 'goodness of fit' between the calculated and observed models was 1.67. The final electron density difference map did not reveal any significant electron density above 0.24 e Å^{-3}.

The final atomic co-ordinates for (2-O) are listed in Table 1. The values of the thermal parameters and of the structure factors are in Supplementary Publication No. SUP 23146 (12 pp.).†

X-*Ray Structure Determination of Red Diethyl* NN′-*Diphenyl*-2,5-*diaminoterephthalate* (2-R).—A crystal 1.0 × 0.6 × 0.01 mm grown by recrystallization from ethyl acetate was used for data collection.

Crystal data. $C_{24}H_{24}N_2O_4$, $M = 404.5$, triclinic, $a = 10.124(5)$, $b = 4.025(1)$, $c = 13.623(8)$ Å, $\alpha = 90.46(4)°$, $\beta = 106.95(4)°$, $\gamma = 99.64(4)°$, $U = 522.6$ Å, $Z = 1$, $D_c = 1.29$ g cm^{-3}, $F(000) = 214$; no systematic absences; space group $P1$ or $P\bar{1}$, the latter confirmed by the results of the analysis. The procedures for determination of the unit cell parameters, data collection, assigning weights and scattering factors were as for (2-O). A total of 1 469 reflections was considered non-zero at the 1.96σ significance level out of 1 721 possible reflections in the 2θ range 2—130°. There was no evidence for crystal deterioration.

TABLE 2

Final atomic co-ordinates for (2-R) in fractions of the unit cell edge [a]

Atom	*X*	*Y*	*Z*
O(1)	−0.351 35(11)	0.252 9(3)	−0.056 88(8)
O(2)	−0.238 04(10)	0.332 8(3)	0.111 13(7)
N(1)	−0.214 50(13)	0.050 8(4)	−0.182 52(9)
C(1)	0.013 48(14)	−0.086 0(4)	−0.094 14(9)
C(2)	−0.108 24(15)	0.029 9(4)	−0.092 73(10)
C(3)	−0.120 94(14)	0.117 2(4)	0.005 07(10)
C(4)	−0.247 42(14)	0.239 8(4)	0.014 07(11)
C(5)	−0.361 50(16)	0.446 4(4)	0.125 33(12)
C(6)	−0.327 20(20)	0.560 0(6)	0.236 08(14)
C(7)	−0.206 36(16)	0.042 7(4)	−0.284 03(11)
C(8)	−0.323 07(18)	−0.113 2(5)	−0.361 86(13)
C(9)	−0.320 76(22)	−0.111 5(6)	−0.463 49(14)
C(10)	−0.203 70(23)	0.036 6(6)	−0.487 60(13)
C(11)	−0.087 68(20)	0.194 3(5)	−0.410 80(13)
C(12)	−0.088 27(17)	0.198 8(4)	−0.309 19(12)
NH(1)	−0.297(2)	0.088(5)	−0.173 0(15)
H(1)	0.026(2)	−0.155(4)	−0.158 5(13)
H(2)	−0.437(2)	0.261(4)	0.106 2(12)
H(3)	−0.383(2)	0.646(5)	0.080 4(12)
H(6)	−0.299(2)	0.380(6)	0.281 1(14)
H(5)	−0.405(2)	0.637(5)	0.246 9(13)
H(4)	−0.248(3)	0.666(8)	0.252 9(18)
H(8)	−0.409(2)	−0.224(5)	−0.338 8(14)
H(9)	−0.402(2)	−0.232(6)	−0.516 7(16)
H(10)	−0.206(2)	0.027(6)	−0.562 1(15)
H(11)	0.004(2)	0.301(5)	−0.424 4(13)
H(12)	−0.009(2)	0.324(5)	−0.256 9(12)

[a] The rest of the molecule can be generated by the centre of inversion at 0, 0, 0.

The structure was solved in space group $P\bar{1}$ using the MULTAN program.[7] After an E map revealed a chemically reasonable six-atom fragment situated about a centre of symmetry alternate Fourier syntheses and block diagonal

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* $R = \Sigma||F_0| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; 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.

least squares refinement revealed the positions of all non-hydrogen atoms. Full matrix least squares refinement incorporating positional and anisotropic temperature parameters for the non-hydrogen atoms gave R 0.099. An electron density difference map revealed the positions of all hydrogen atoms; further least squares refinement including positional parameters for all atoms, isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for the non-hydrogens resulted in R 0.043 and R_2 0.060 on the non-zero data. The ' goodness of fit ' between the calculated and observed models was 1.57. A final electron density difference map revealed no significant electron density above 0.12 e Å^{-3}.

The final atomic co-ordinates for (2-R) are listed in Table 2. The values of the thermal parameters and of the structure factors are in SUP 23146.

RESULTS AND DISCUSSION

It had been reported by Liebermann[3] that the *NN'*-diphenyl compound (2) gave on crystallization an orange modification which on heating to 100 °C was converted into a red form. It was found in the present work that, although many common solvents gave the red form (2-R) in agreement with Liebermann, and that rapid crystallization from a few solvents such as pyridine, cyclohexane, methylene dichloride, methanol, or acetone gave under the appropriate conditions an orange powder, the orange form was extremely unstable and rapidly changed to the red form even at room temperature; no orange modification with the stability reported by Liebermann was ever observed. Slow evaporation of a benzene solution of (2) at room temperature did give orange crystals (2-O) sufficiently stable to work with when kept at temperatures not greater than 0 °C or in an atmosphere of benzene. These were found to be a complex of (2-O) and benzene in a ratio of 1 : 1 and their *X*-ray crystal structure and reversible loss of benzene and conversion into (2-R) will be the subject of the remainder of this paper. We can only speculate as to the source of the disagreement between our work and that of Liebermann; perhaps in his laboratory there was nucleation of a different more stable orange form.

Crystals of (2-O) when allowed to stand at room temperature turned red and lost benzene completely within 24 h. The percentage loss of benzene followed gravimetrically was approximately linear with time for the first 30% (in *ca.* 1 h) although, as could be expected, there was some variation in the behaviour of individual samples and between crystals of different external shapes (see Figure 1). Observation of single crystals on the stage of a polarizing microscope showed a process that, within the limits of resolution of the microscope, was clearly heterogeneous, *i.e.* reaction began at one or more nucleation sites (often only one) and spread throughout the crystal as had been observed with the conversion of (1-Y) into (1-O) described previously.

There are however, several important differences between the two cases. The reaction front during the conversion of (2-O) into (2-R) was followed by an orange phase which no longer showed extinction on rotation of the crystal between crossed polarizing filters. A second front then developed separating the orange phase from the red (2-R) which was finally formed. Powder photography showed the rearranged product to be identical with (2-R) obtained by crystallization.

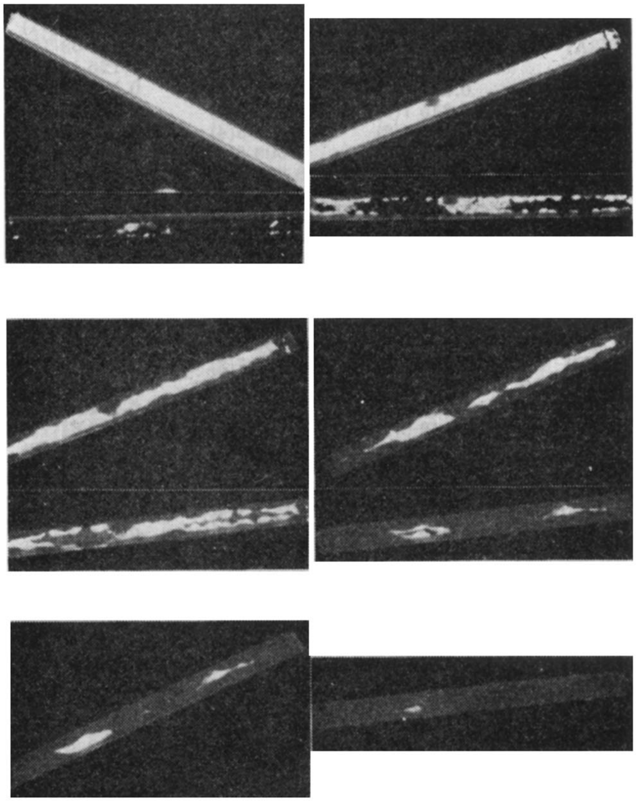
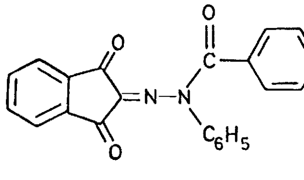


FIGURE 1 A single crystal of (2-O) rearranging with loss of benzene to (2-R) at room temperature. In the top left is an orange crystal at *t* 0 (crystal diagonal in the photograph). The crystal is between crossed polarizing filters and in the transmission position. Immediately below that photograph is one (crystal horizontal) taken at the same time with the same crystal in the extinction position. It will be noted that, although the crystal appears clear in the transmission position, when rotated to the extinction position orange areas (which appear white in the black-and-white photograph) which no longer extinguish have begun to appear. The pair of photographs (top right) taken after 15 min shows the appearance of a red region (black in the black-and-white photograph) due to the formation of (2-R). However, in the extinction position (immediately below) substantial yellow areas of the crystal no longer extinguish polarized light due to the formation of the benzene-free phase of (2-O). The two middle pairs of pictures were taken in the same way after 30 and 45 min and the bottom pictures (which are no longer accompanied by a photograph taken in the extinction orientation) were taken after 60 and 75 min

The nature of the intermediate orange phase is not easily investigated directly because of the speed of the reaction and the small fraction of the crystal existing in this transient phase at a particular time. While the initial process could be a phase transformation from the starting benzene complex (2-O) to a polymorphic orange benzene complex, it seems much more likely that the initial process is loss of benzene to give a solvent-free orange crystalline form. Our previously mentioned observation of short-lived orange powders on recrystallization of (2) from a variety of solvents supports the hypothesis that such a form is a reasonable intermediate.

A second difference between the conversion of (2-O) into (2-R) and that of (1-Y) into (1-O) is that the reaction of (2) is readily reversible although the reverse product is microcrystalline. The reversible loss of solvent is at least superficially related to the interconversion of (yellow) indanetrione 2-(*N*-*p*-t-butylbenzoyl-*N*-phenylhydrazone)-acetone (3-Y) into the red acetone-free product (3-R),[8] a process which was also reversible, but which lacks a second yellow phase.



(3)

The nucleation of the reaction of single crystals of (2-O) occurred most frequently at the side or end faces of the crystal. The nucleation was much more easily influenced by identifiable external influences than the rearrangement of (1-Y) to (1-O) or of the other heterogeneous transformations we have studied;[4,9] nucleation by mechanical deformation was also sensitive to the presence of the vapour of acetone, ethanol, or even water.

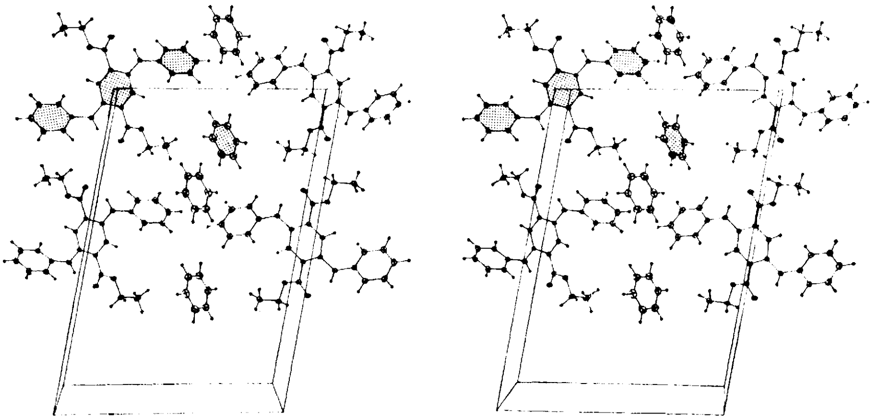


FIGURE 2 The structure of the crystal of (2-O). The origin is at the top left-hand rear corner. The *a* axis is horizontal, the *c*-axis is near vertical, and the *b* axis is almost normal to the plane of the paper. The reference molecule A, which is centred at 0, ½, 0, has the phenyl rings shaded as has the reference benzene solvate molecule. The reference molecule B is not shown but the molecule related by a unit transition in *a* is shown at the top right of the picture

Structural Change in the Interconversion of (2-O) *and* (2-R).—The structures of (2-O) and 2-R) are shown in Figures 2 and 3. Bond lengths and angles in both structures are given in Figures 4 and 5. The structures of the individual molecules in the two crystals are shown in Figure 6. It is evident that although little change in molecular conformation is required for progression from (2-O) to (2-R), even neglecting the complication of the loss of solvent, a major repacking of the crystal is required. Thus, although the structure of (2-R) can be constructed by translation of molecules with a single conformation and a single spatial orientation, (2-O) has as its basic structural unit a pair of molecules related by an approximate two-fold rotation about the axis of the benzene channel. It follows that in the transformation of (2-O) to (2-R) there is required not only loss of the benzene molecules but also a total repacking of the structure. In the previously studied example of the loss of acetone from an indanetrione phenylhydrazone–acetone complex there was a strong structural relationship between the starting and product crystals;[8] no such relationship exists here.

X-Ray Crystal Structures and Molecular Packing of (2-O) *and* (2-R).—The structure of (2-O) in space group $P2_1/c$ with four centrosymmetric molecules plus four molecules of benzene per unit cell has as it most interesting structural features the way in which the two independent molecules of the terephthalate are related and the manner of incorporation of the benzene molecules. The two terephthalate rings are stacked one above the other with the two central benzene rings almost parallel (the angle between the best planes is 2.3°) and the rings are related by almost a two-fold axis. The benzene molecules were located (including the hydrogen atoms) and found to be oriented almost perpendicular to the *N*-phenyl rings of the two independent molecules of terephthalate. There are no short contacts between the benzene molecule and the surrounding molecules of (2) suggestive of any specific guest–host interactions. There are no intramolecular hydrogen bonds and no carbonyl–carbonyl interactions

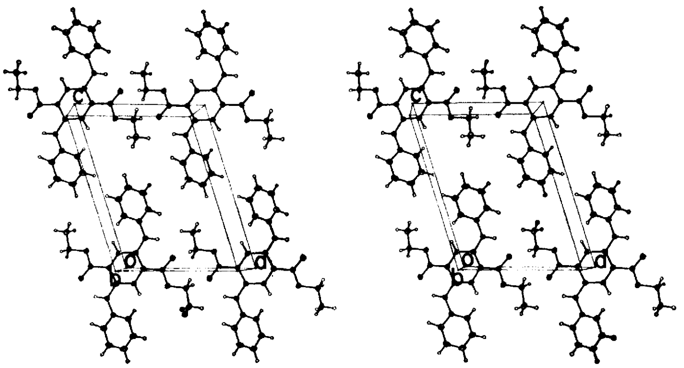


FIGURE 3 Stereoscopic view of the packing of molecules in the (2-R) crystal. The reference molecule is at the bottom left-hand corner of the unit cell with the atoms in the asymmetric unit whose co-ordinates are given in Table 2, mostly lying outside the cell

as had been found in (1-Y). The benzene rings are thus contained in infinite channels parallel to the *b*-axis of the crystal (Figure 7). If the channel is assumed to be cylindrical the average diameter is 6 Å; there are constrictions in the channel, however, to a diameter of 4 Å. Since the benzene molecule has a thickness of *ca.* 3.7 Å and a diameter of *ca.* 6 Å, its passage through the channel is impeded unless there is appreciable distortion of the crystal.

The structure of (2-R), since it belongs to space group $P\bar{1}$ with one molecule per unit cell, is the simplest possible with stacks of molecules overlapping as shown in Figure 8. The distance between planes of the terephthalate rings is 7 Å. Again there seem to be only van der Waals forces holding the structure together.

Conclusions.—The most striking aspect of the present transformation is that, possibly because of the extensive reordering which is required to change (2-O) to (2-R), the initial product of loss of benzene is not (2-R) but presumably a second crystalline form of (2-O); it might be inferred that the orange benzene-free intermediate is structurally more closely related to (2-O) than to (2-R) but the instability of (2-O) has prevented us from investigating this question.

The colour change associated with the take-up of benzene vapour by the benzene-free crystals of (2-R)

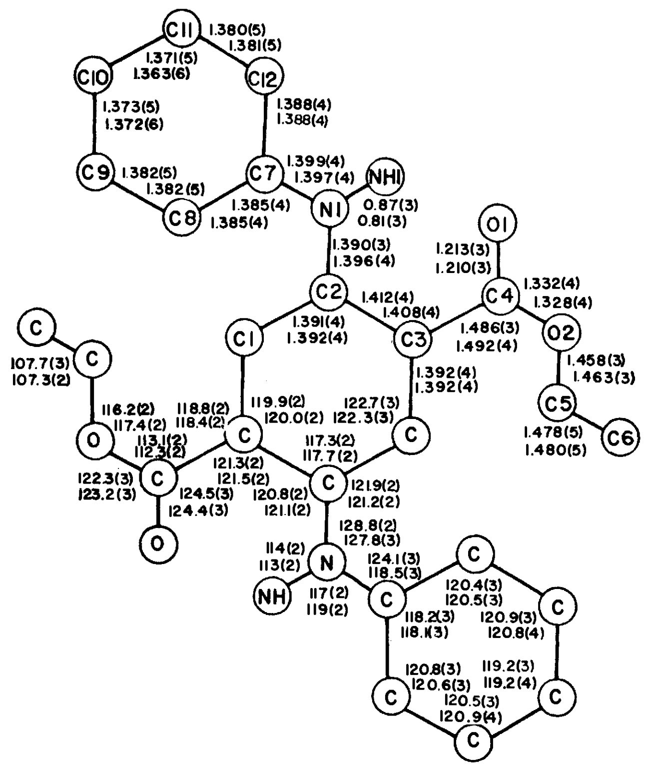


FIGURE 4 Bond lengths (Å) and angles (°) for the two centrosymmetric molecules in the crystal of (2-O)

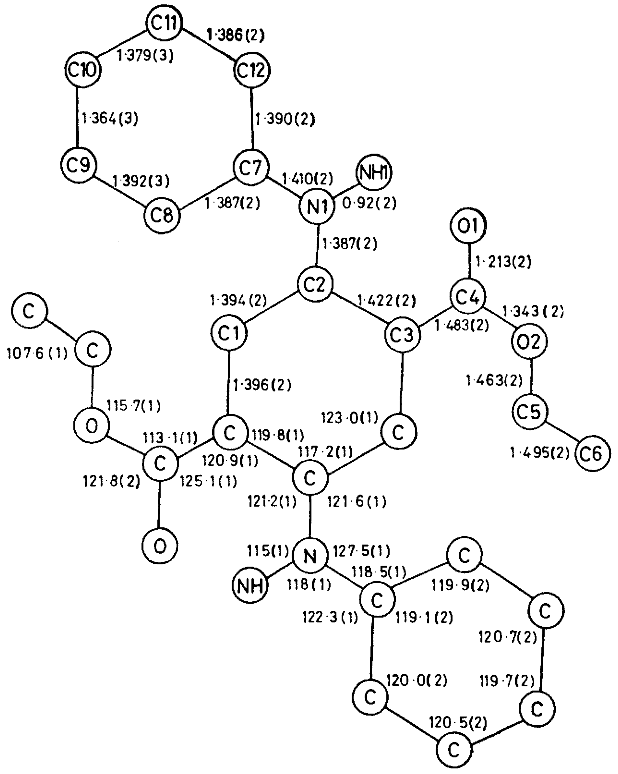


FIGURE 5 Bond lengths (Å) and angles (°) for the centrosymmetric molecule in the crystal of (2-R)

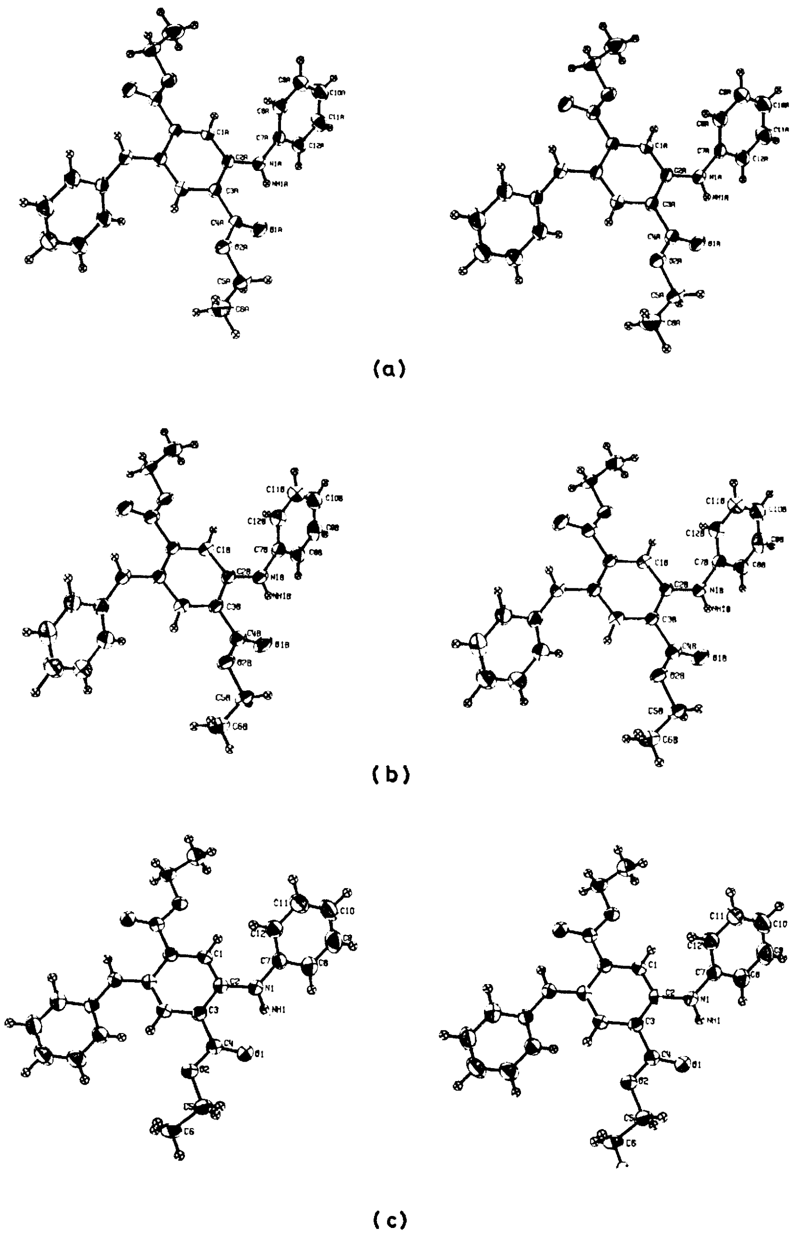


FIGURE 6 Stereoscopic views of (*a*) molecule A in the crystal of (2-O); (*b*) molecule B in the crystal of (2-O); (*c*) the molecule in the crystal of (2-R)

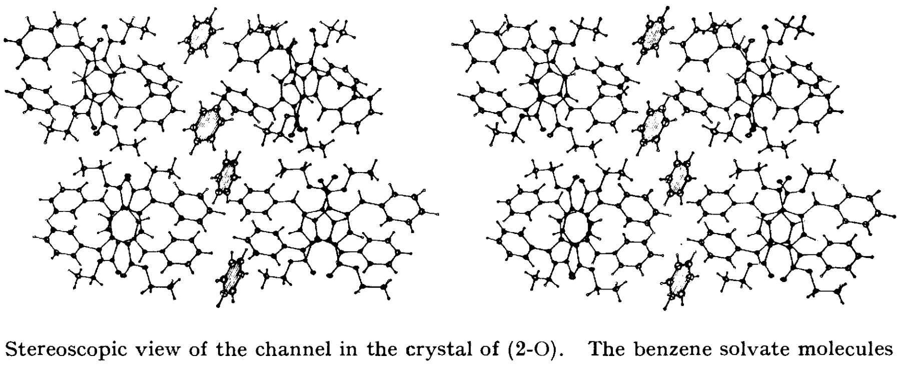


FIGURE 7 Stereoscopic view of the channel in the crystal of (2-O). The benzene solvate molecules are shaded

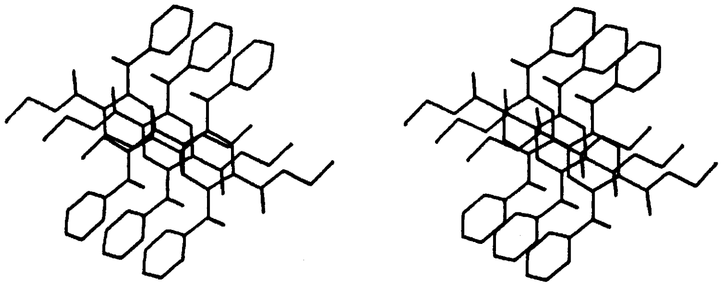


FIGURE 8 Stereoscopic view of the overlap of molecules of (2) in the crystal of (2-R). The view is virtually along the *b*-axis

provides an interesting example of a reversible gas–solid reaction which, since it is accompanied by a colour change, could have analytical applications.

Another point of unusual interest in this study is the ease with which the nucleation of the transformaton of single crystals of (2-O) to (2-R) can be influenced by external stimuli.

It is hoped that further investigations of this and other such changes in the solid state will lead to results of both practical and theoretical interest.

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