An Unusual Photo-induced Conformational Polymorphism: a Crystallographic Study of Bis(*p*-methoxy)-*trans*-stilbene

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A novel example of a photo-induced single-crystal to single-crystal phase transformation is described for the title compound; the accompanying change in molecular conformation is rationalised in terms of an intermediate excimeric state.

The photochemical behaviour of *trans*-stilbenes has long been of interest to solid state chemists, not least because when crystals of the parent molecule are irradiated with u.v. light, *cis* ⟷ *trans* isomerisation occurs, but not [2 + 2] cycloaddition of the exocyclic double bond. Even the expedient of forming an inclusion complex of stilbene, with, for example, tri-ortho-thymotide,[1] does not force the guest in a packing mode which is conducive to dimerisation under topochemical control. On the other hand, when dichloro-substitution is introduced in the *trans*-stilbene framework, a reactive motif is obtained, and dimerisation follows.[2] Furthermore, in a study of the factors which determine the crystallinity of the reaction product in a solid state photochemical reaction, it has been shown[3] (in the case of the 2-benzyl-5-benzylidenecyclopentanone series, BBCP) that a prerequisite of a single-crystal to single-crystal type of dimerisation[4—6] may be a sidegroup which is flexible. Such a flexible group also allows the formation of crystalline binary solid solutions, when the constituent molecules differ only in the nature of the substituent within the flexible group.[7] The photochemical behaviour of the title compound (**1**) was therefore studied. The introduction of the methoxy group, it was hoped, would introduce 'flexibility' within the molecule and that a reactive structure would result which would yield a highly crystalline product. It transpires, however, that no chemical reaction accompanies u.v. irradiation, but rather that a novel photo-induced phase transformation takes place with significant changes in molecular conformation.

The crystal structure of (**1**) was determined; the same crystal was subsequently irradiated on the goniometer head of an *X*-ray camera for 10 days (with continuous crystal rotation to achieve uniform exposure), using a 100 W low-pressure Hg lamp. The crystal structure of the product crystal (**2**) thus prepared, was then determined. Data collection for crystal (**2**) was started as soon as possible after the cessation of irradiation. I.r. spectra of the title stilbene were taken before and after irradiation (KBr pressed pellet). The only major difference between the two spectra, was the diminution in the intensity of the 1609 cm^{-1} peak in the spectrum of (**2**); this peak has been assigned to the exocyclic double bond stretch.

Full *X*-ray structural data was obtained using an Enraf–Nonius CAD-4 four-circle diffractometer with Cu-K_α radiation, in the manner that has been given elsewhere.[8] Both structures were solved by direct methods, and refined by full-matrix least-squares techniques. All calculations were carried out using SHELX-76 (G. M. Sheldrick), PLUTO-78

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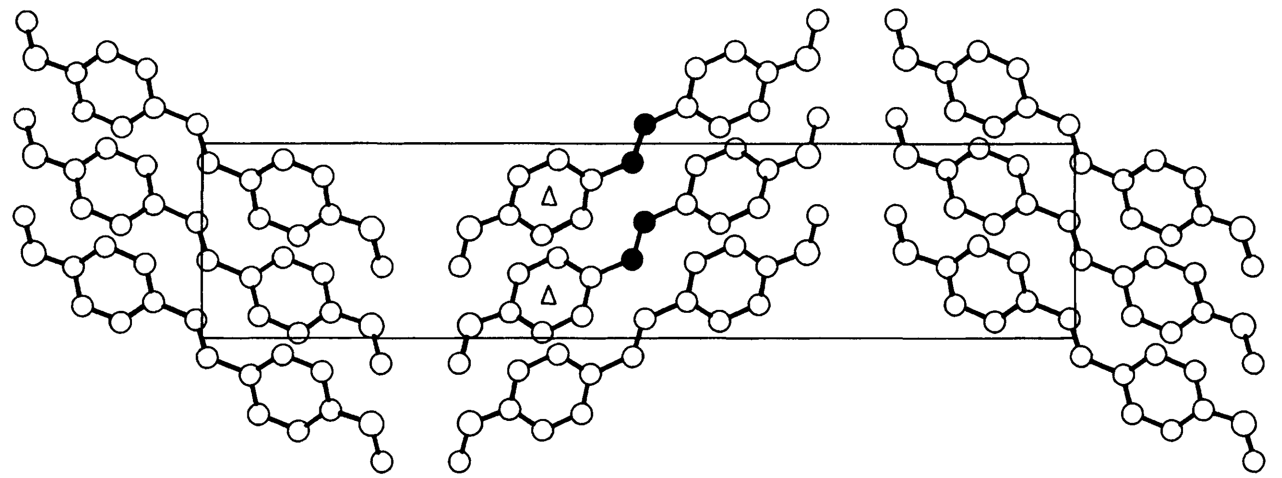

Figure 1. Crystal structure of (**1**) viewed along the *c* axis. The molecules marked △ are the nearest neighbours. The double bonds in these two molecules are marked.

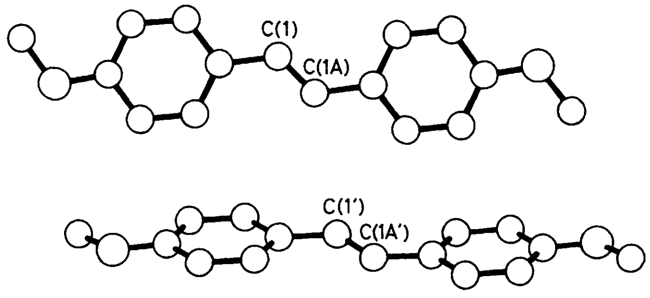

Figure 2. The nearest neighbour pair in (**1**) viewed along a low symmetry direction.

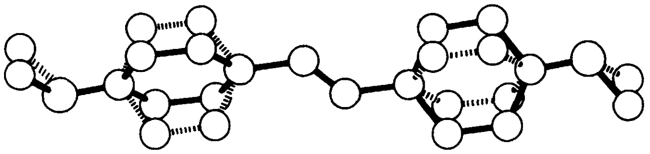

Figure 3. The molecular structure of (**2**).

(W. D. S. Motherwell), and private programs, on an IBM-3081 computer (University of Cambridge).‡

Compound (**1**) packs in spacegroup *Pbca*, the asymmetric unit comprising half the molecule; the centre of the exocyclic double bond is located on a crystallographic centre of symmetry. Conjugation operates throughout the molecule; the molecule is therefore flat. Figure 1 shows the crystal structure of (**1**) viewed along the *c* axis. Closest intermolecular contact for the exocyclic double bond is for the *a* glide-related molecules. However, as may be seen from Figure 2, the two double bonds are not parallel; C(1) · · · C(1') is 4.10 Å, C(1A) · · · C(1A') 5.10 Å, these distances being too long for a topochemical reaction.[3—6] Packing in this crystal is very dense, with the double bond of each molecule having short (<4.60 Å) contacts with double bonds on four other neighbouring molecules. In addition, there are in (**1**) a number of other short (<4.0 Å) C · · · C contacts between the central and the four surrounding molecules. In contrast, in BBCP[3] the exocyclic double bond has a closest contact of 4.0 Å, with the second nearest one being in excess of 5.0 Å.

Irradiation of a single crystal of (**1**) results in a change of spacegroup, but the single crystal character of the specimen is not lost. The irradiated crystal (**2**) packs in spacegroup $P2_1/n$, with the centre of the exocyclic double bond coinciding with a crystallographic centre of symmetry. Consequently, the asymmetric unit corresponds to half the molecule. Within the asymmetric unit, the methyl carbon, as well as the phenyl group, were refined at two different positions, each with a refined occupancy factor of 0.5. The carbon atoms of the phenyl group bonded to the two substituents (double bond and methoxy), the oxygen, and the double bond carbon, refined to a single position. The two positions of the phenyl group within the asymmetric unit subtend a dihedral angle of 63°. This means that rotation round the single bonds linking the central double bonds with the phenyl rings has resulted in a molecule which is no longer planar. Figure 3 shows the molecular structure of (**2**), and Figure 4 the crystal structure viewed along the *c* axis. Crystals (**1**) and (**2**) are related topotactically, with the *b* axes coinciding in length and direction. The *c* axis in (**1**) is parallel to *c* in (**2**), but the lengths are not equal. Comparison of Figures 1 and 4 shows the two packing motifs to be similar, with no evidence for dimerisation in (**2**). The nearest double bond contacts are for molecules related by translation along *c* (4.85 Å). Although the double bonds are now parallel, they are still too far away for a topochemical [2 + 2] cycloaddition.

When considered as an example of conformational isomerisation, the photochemical transformation of (**1**) into (**2**) may be rationalised in the following way. Compound (**1**) possesses an extended conjugation system and is therefore likely, upon u.v. irradiation, to form excimers. Excimer formation

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‡ *Crystal data:* (**1**) $C_{16}H_{16}O_2$, M = 240.29, orthorhombic, a = 6.226(1), b = 27.976(2), c = 7.424(1) Å, U = 1293.1 Å^3, $F(000)$ = 512, D_c = 1.234 g cm^{-3}, Z = 4, μ(Cu-K_α) = 5.58 cm^{-1}, λ = 1.54178 Å, crystal size = 0.50 × 0.30 × 0.10 mm, $3 < \theta < 70°$, total data unique = 1026, total data observed = 556, significance test = $F_0 > 2\sigma(F)$, refined parameters = 106, maximum peak in last difference Fourier map = 0.20 e Å^{-3}, R = 0.0546. (**2**) monoclinic, a = 4.846(1), b = 27.974(2), c = 4.845(1) Å, β = 100.04(1)°, U = 646.7 Å^3, $F(000)$ = 256, D_c = 1.234 g cm^{-3}, Z = 2, μ(Cu-K_α) = 5.58 cm^{-1}, $3 < \theta < 70°$, total data unique = 1052, total data observed = 670, significance test = $F_0 > 1.5\sigma(F)$, refined parameters = 127, maximum peak in last difference Fourier map = 0.30 e Å^{-3}, R = 0.0771. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

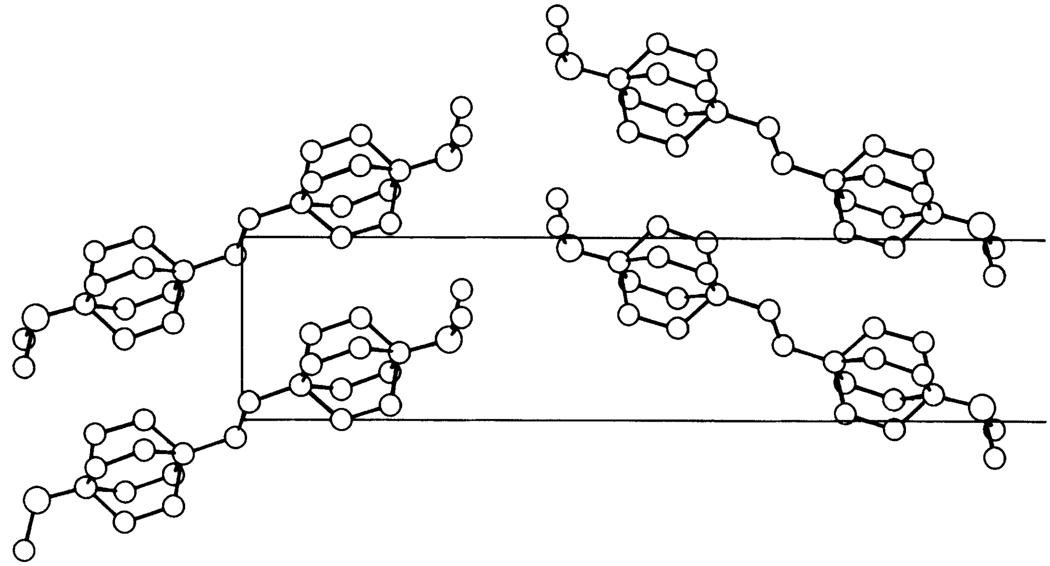

Figure 4. Crystal structure of (**2**) viewed along the *c* axis.

requires the approach of two molecules from their equilibrium position. Ordinarily, the excimer can relax back to the ground state allowing its constituent monomers to revert to their original positions. In (**1**) however, the molecules are packed rather closely together, and this final step may not be possible. The ground state molecules of (**1**) take up different positions to those from which they started, resulting in the packing in structure (**2**). In order to accommodate this, a conformational change occurs to give the molecule as in (**2**), in which the phenyl rings are no longer coplanar.

The asymmetric unit of (**2**), is, as in (**1**), half the molecule, but in the former the phenyl group is resolved at two different positions. This indicates that the change of conformation is accompanied by the onset of disorder, brought about, presumably, by steric considerations. Nearest neighbours in (**1**) subtend an intermolecular dihedral angle of 63°. Excimer formation, requires the two participating molecules to be parallel. This is reflected in the fact that nearest neighbours in (**2**) are related by translation.

There is some preliminary evidence that on standing for a long period at room temperature, (**2**) reverts to (**1**). Detailed spectroscopic measurements and other investigations will be reported elsewhere.

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References

1 R. Arad-Yellin, B. S. Green, S. Brunie, M. Knossow, and G. Tsoukaris, *Mol. Cryst. Liq. Cryst.*, 1979, **50**, 275.
2 M. D. Cohen, B. S. Green, Z. Ludmer, and G. M. J. Schmidt, *Chem. Phys. Lett.*, 1970, **7**, 486.
3 H. Nakanishi, W. Jones, J. M. Thomas, M. B. Hursthouse, and M. Motevalli, *J. Phys. Chem.*, 1981, **85**, 3636.
4 C. R. Theocharis, G. R. Desiraju, and W. Jones, *J. Am. Chem. Soc.*, 1984, **106**, 3606.
5 C. R. Theocharis, Ph.D. Thesis, University of Cambridge, 1982.
6 C. R. Theocharis, W. Jones, M. Motevalli, and M. B. Hursthouse, *J. Cryst. Spec. Res.*, 1982, **12**, 377.
7 W. Jones, C. R. Theocharis, J. M. Thomas, and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1983, 1443.
8 C. R. Theocharis and W. Jones, *J. Chem. Soc., Faraday Trans. 1*, in the press.