

Isomerization Processes in Inclusion Compounds: Xylenes in Deoxycholic Acid

F. GALLESE, A. GUARINO and E. POSSAGNO

Istituto di Chimica Nucleare del CNR, CP 10, I-00016, Monterotondo Stazione, Roma, Italy.

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Abstract. The isomerization processes induced by UV photons in inclusion compounds of the host–guest type are examined, with special attention to the photophysics of the energy transfer process between the host and the guest, as well as to the influence of the host molecular cavity symmetry and the guest molecular symmetry. In particular, the experimental study has been carried out on the isomerization processes of *p*-, *m*-, and *o*-xylene inside the molecular cavities of deoxycholic acid. The results have been compared with those obtained by irradiating the xylenes in an inert solution of hexane. The main difference is the elimination of by-products when the photochemical process is carried out in the solid state inclusion compound; however, the high purity of the isomerization product corresponds to a decrease in its yield with respect to the reaction in solution, due to the energy transfer process from the host to the guest moiety.

Key words. Host–guest inclusion compound, *p*-, *m*-, *o*-xylene, deoxycholic acid, symmetry factor, energy transfer, photophysical factor, crystal structure.

1. Introduction

One of the most intriguing aspects of solid state photochemistry is the theoretical and experimental study of reaction pathways; for many years, studies have been devoted to the isomerization processes which occur inside the molecular cavities formed by compounds such as deoxycholic acid, Ni(II)-Werner complexes, TOT, cyclodextrins, etc. [1]. In particular, the following isomerization processes have been studied:

- (i) valence isomerization of norbornadiene and its homologous to quadricyclenes;
- (ii) *cis*–*trans* isomerization of stilbenes and cinnamates;
- (iii) position isomerization of xylenes.

The first isomerization process was studied in order to exploit the potentialities of a well-known [2] photochemical process useful for the storage of solar energy:



A special device was assembled to test this reaction on a column formed by deoxycholic acid: it is worth observing that the main difference between this process carried out in solution and as an inclusion compound in the solid state is that in the latter case the major product is the isomer [3], with only traces of by-products, which are formed in large yields in solution.

The *cis-trans* isomerization process was carried out on *cis* and *trans* stilbene and *cis* and *trans* methylcinnamate, acting as guests, and many compounds acting as hosts, i.e. TOT, cyclodextrins, Ni(II)-Werner complexes and deoxycholic acid [4].

The previously reported isomerization processes have shown how the photochemical processes in these specific solid state compounds formed by host-guest inclusion complexes are strongly dependent on two factors, i.e. the photophysical factor which determines the energy transfer between the excited host and the guest [5], and the symmetry factor which determines the relationship between the symmetry of the molecular cavity of the host and the molecular symmetry of the guest [6]. The occurrence of the isomerization reaction and the yield of the reaction are strongly influenced by these two factors, which may be studied on the basis of the photophysical properties of the molecules involved and by simulating the structure of the inclusion compound by computer graphics with a programme based on the minimum van der Waals' energy, provided that crystallographic parameters are known for the complex involved.

The present work refers to the isomerization of *o*-, *m*- and *p*-xylene in deoxycholic acid and it has been studied in order to observe the influence of the molecular cavity on the isomerization reactions that imply 1,2- and/or 1,3-methyl shifts as well as the formation of addition and disproportionation products when the process is carried out in solution [7].

2. Experimental

Gas-chromatographically pure *o*-, *m*- and *p*-xylenes were included in deoxycholic acid (DCA) according to the usual procedure [3]. Their content and purity inside the DCA channels were established accurately by VPC employing columns of bentone-didecylphthalate at 60°C with a flame detector, on a Carlo Erba gas chromatograph.

The crystals of the various inclusion compounds were irradiated by UV photons at increasing doses, from 1.8×10^{19} up to 2.6×10^{20} quanta cm^{-2} .

The same xylenes were irradiated by UV photons at the same doses in a solution of hexane (gas-chromatographically and spectroscopically pure).

After the irradiation, the inclusion compound crystals were dissolved in hexane and analysed by VPC on the same columns described previously. An analogous procedure was employed for the xylenes irradiated in hexane solution.

Single crystals of the DCA-xylene inclusion compounds were subjected to X-ray diffractometric analysis in order to solve the structures and to determine the shape of the molecular cavities of the host and the specific position of the guest [8].

Suitable crystals of the DCA/*o*-, *m*-, *p*-xylene complex were grown at room temperature by slow evaporation of methanol solutions of DCA and xylenes. They were small, needle-like and colourless.

Preliminary measurement of the unit-cell dimensions and observations of the diffraction symmetry and of the systematic absences were made by photographic methods.

Diffraction data were collected using a Syntex diffractometer, Cu-K α radiation and graphite monochromator.

Data were corrected for Lp factors but no corrections for extinction or absorption were applied.

3. Results and Discussion

The results of the various irradiations are summarised in Table I.

The main difference between irradiation in solution and as a solid state inclusion compound is the ratio isomerization/disproportionation for the two cases. In fact, the disproportionation reaction occurs by means of a bulky intermediate whose formation is practically inhibited by the molecular cavity of DCA. No such problems exist for the isomerization reaction which is a molecular rearrangement and consequently occurs either in solution or inside the cavities of the host.

As shown in Figures 1–3, there is a significant formation of toluene and pseudocumene starting from *o*-, *m*- and *p*-xylene in hexane solution. In any case, it may be observed that, at increasing doses, the toluene yield decreases and the pseudocumene yield increases.

The 1,2-methyl shift yield in the case of *o*-xylene and *m*-xylene is significantly increased by irradiating the xylenes in solution with respect to the same isomerization inside the DCA molecular cavities, at any dose.

The 1,3-methyl shift yield is low both in solution and in the crystals of the inclusion compounds.

As shown in Figure 4, the isomerization process proceeds inside the host cavities. For *m*-xylene 1,2-methyl shifts give the *o*- and *p*-isomers, with a relatively higher yield of the *p*-isomer, analogous to what happens in hexane solution: i.e. no steric hindrance affects the isomerization process inside the DCA molecular cavities, the lower yield with respect to the hexane solution being a consequence of the lower excitation energy absorbed by the *m*-xylene embedded inside the DCA molecular cavities.

In the case of *o*-xylene, as shown in Figure 5, the 1,2-methyl shift represents the main isomerization product, i.e. the *m*-isomer; the *p*-isomer is formed with much lower yield and practically in a similar amount to that obtained in solution, at any dose, again showing that no hindrance to these processes occurs inside the DCA cavities.

The isomerization process for *p*-xylene in DCA, shown in Figure 6, gives rise to a larger yield of *m*-isomer, as happens in solution; however, at increasing doses, this yield decreases with a simultaneous increase of the *ortho* isomer: it seems reasonable to postulate the occurrence of a secondary reaction which involves the *m*-isomer produced.










The X-ray analysis undertaken to determine the structures of these DCA-xylene complexes elucidate the host-guest interactions that allow the position isomerization process [8].

The crystal data of the inclusion compounds of *o*-, *m*-, and *p*-xylene in DCA are summarised in Table II.

The choleic acid crystal structures so far studied can be grouped into three crystal systems: orthorhombic, tetragonal and hexagonal [9].

All the orthorhombic crystals belong to the $P2_12_12_1$ space group and they have two axes almost equal, one of $\approx 26.5 \text{ \AA}$ (the longest) and a second of $\approx 13.5 \text{ \AA}$,

Table I. UV irradiation of xylenes in solution

| Irradiation dose (quanta cm^{-2}) | Starting compound <i>p</i> -xylene | | | <i>m</i> -xylene | | | <i>o</i> -xylene | | | |
|--|---|---|--|---|---|---|---|--|--|-----|
| |  |  |  |  |  |  |  |  |  | |
| 1.8×10^{19} | — | 3.4 | 4.6 | 0.7 | — | 1.4 | 0.9 | — | 0.8 | 1.6 |
| 3.6×10^{19} | — | 7.5 | 6.7 | 0.6 | 2.0 | — | — | 1.5 | 0.5 | — |
| 7.8×10^{19} | 0.2 | 0.5 | 2.3 | 4.1 | 8.6 | — | 1.6 | 4.9 | 0.8 | 1.1 |
| 1.7×10^{20} | 0.4 | 1.2 | 13.2 | 5.7 | 10.7 | — | 4.9 | 6.3 | 0.7 | 7.6 |

Yields of products*

| Irradiation dose (quanta cm^{-2}) | Starting compound <i>p</i> -xylene | | | <i>m</i> -xylene | | | <i>o</i> -xylene | | |
|--|---------------------------------------|-------------|-------------|------------------|-------------|-------------|------------------|-------------|-------------|
| | <i>ortho</i> | <i>meta</i> | <i>para</i> | <i>ortho</i> | <i>meta</i> | <i>para</i> | <i>ortho</i> | <i>meta</i> | <i>para</i> |
| 5.4×10^{19} | 0.2 | 2.0 | — | 1.4 | — | 3.4 | — | 0.8 | 0.4 |
| 1.0×10^{20} | 0.2 | 2.1 | — | 2.2 | — | 3.2 | — | 1.3 | 0.7 |
| 1.6×10^{20} | 0.3 | 1.9 | — | 1.9 | — | 2.0 | — | 1.6 | 0.7 |

(*) Calculated as per cent of transformation of the starting compound.

UV irradiation of xylenes + DCA

| Irradiation dose (quanta cm^{-2}) | Starting compound <i>p</i> -xylene | | | <i>m</i> -xylene | | | <i>o</i> -xylene | | |
|--|---------------------------------------|-------------|-------------|------------------|-------------|-------------|------------------|-------------|-------------|
| | <i>ortho</i> | <i>meta</i> | <i>para</i> | <i>ortho</i> | <i>meta</i> | <i>para</i> | <i>ortho</i> | <i>meta</i> | <i>para</i> |
| 5.4×10^{19} | 0.2 | 2.0 | — | 1.4 | — | 3.4 | — | 0.8 | 0.4 |
| 1.0×10^{20} | 0.2 | 2.1 | — | 2.2 | — | 3.2 | — | 1.3 | 0.7 |
| 1.6×10^{20} | 0.3 | 1.9 | — | 1.9 | — | 2.0 | — | 1.6 | 0.7 |

(*) Calculated as per cent of transformation of the starting compound.

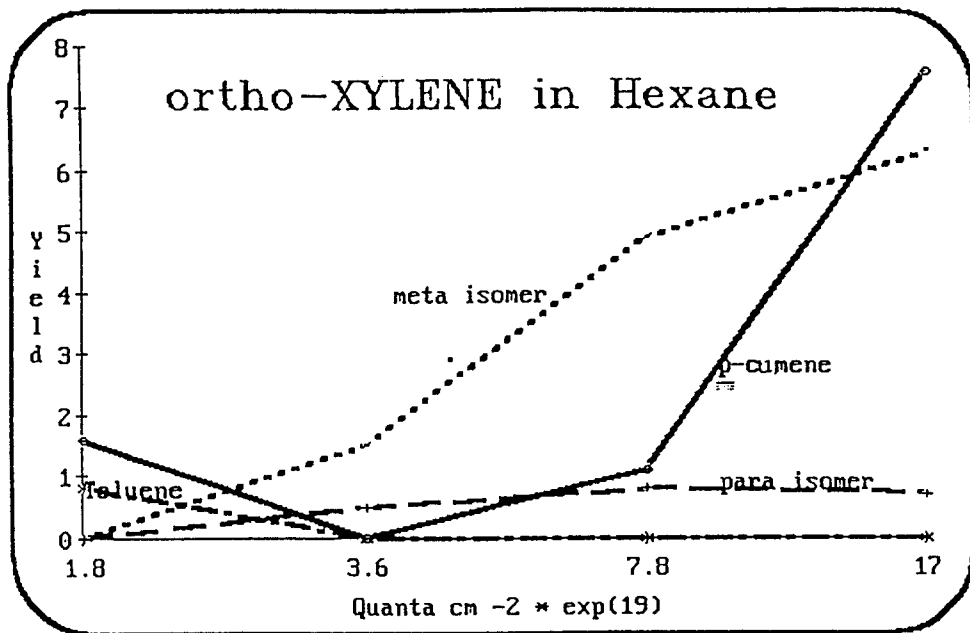


Fig. 1. Yields of products formed during UV irradiation of *o*-xylene in hexane vs. irradiation dose.

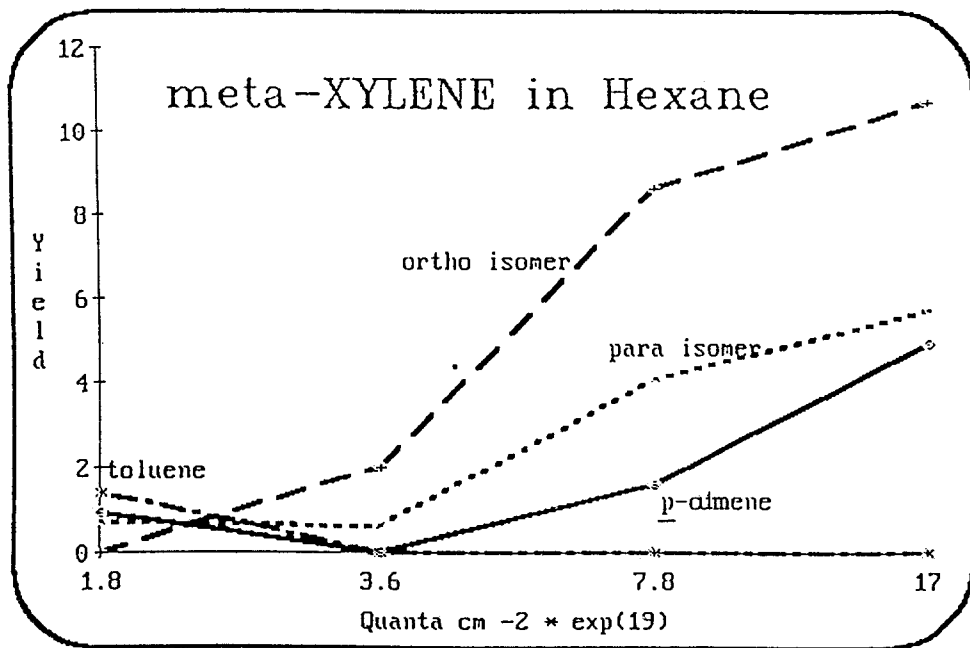


Fig. 2. Yields of products formed during UV irradiation of *m*-xylene in hexane vs. irradiation dose.

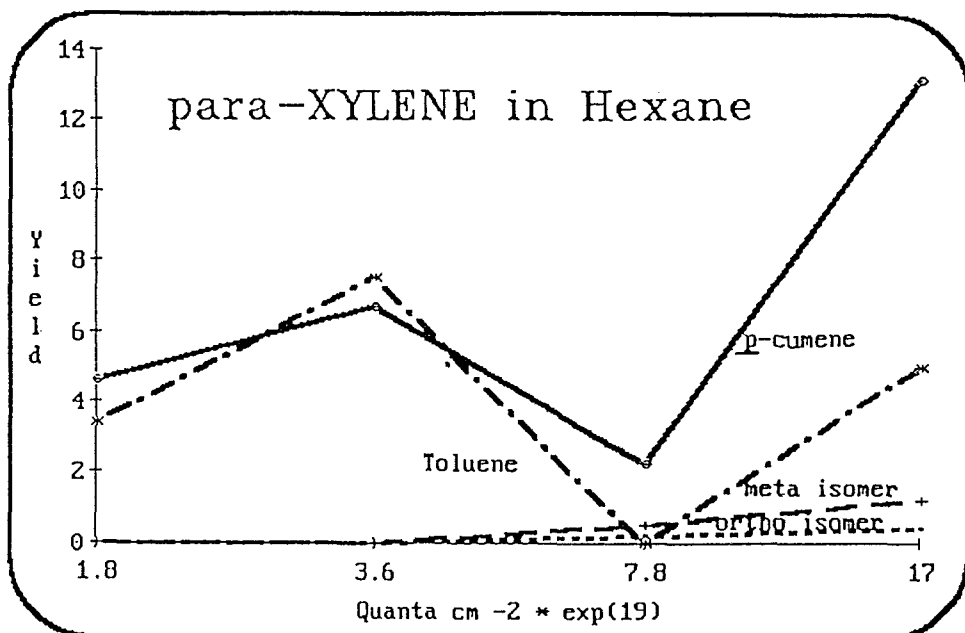


Fig. 3. Yields of products formed during UV irradiation of *p*-xylene in hexane vs. irradiation dose.

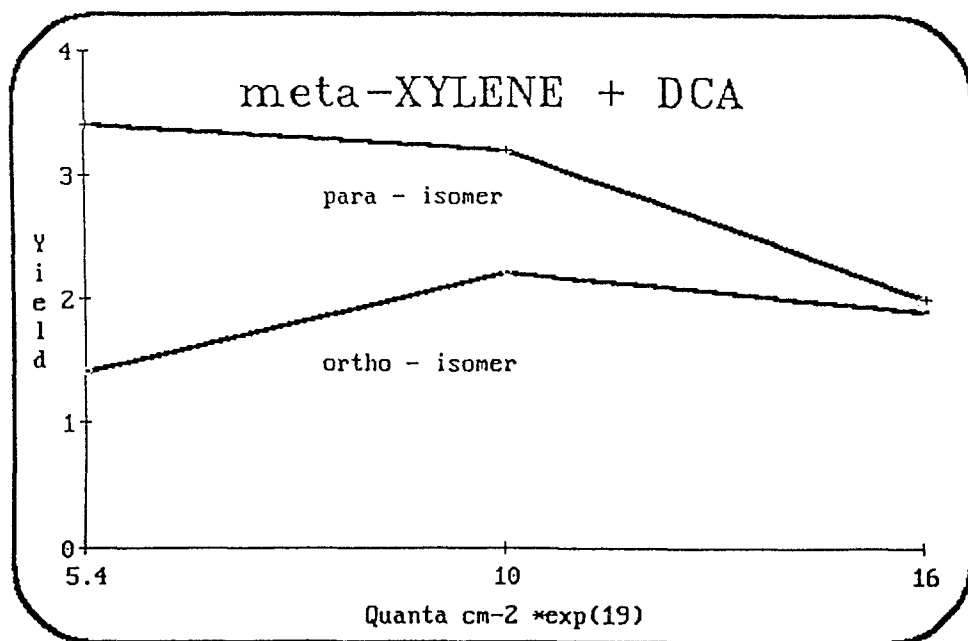


Fig. 4. Yields of products formed during UV irradiation of *m*-xylene in DCA vs. irradiation dose.

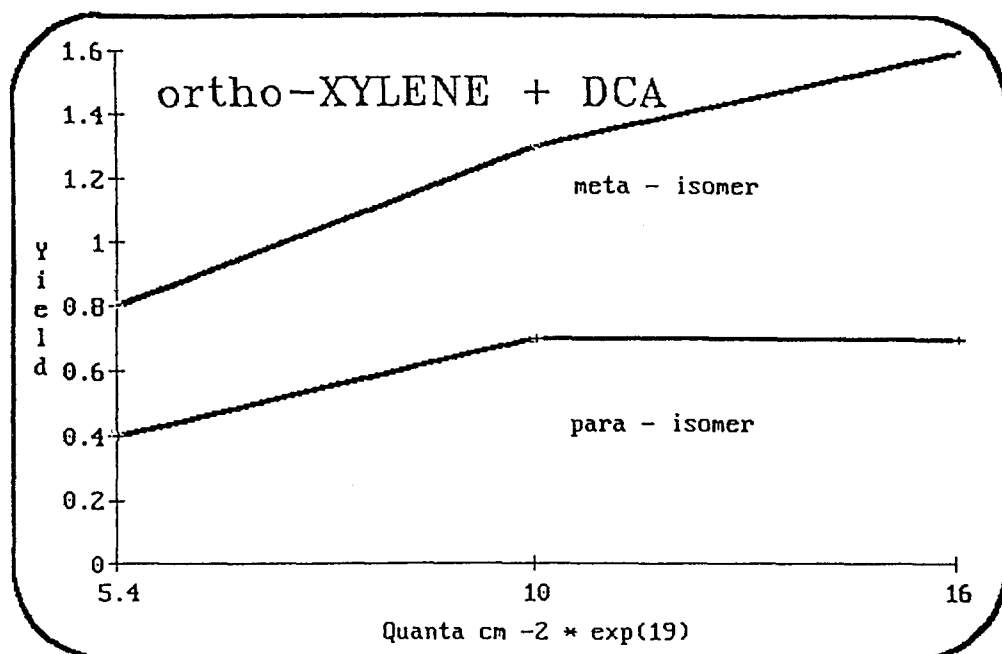


Fig. 5. Yields of products formed during UV irradiation of *o*-xylene in DCA vs. irradiation dose.

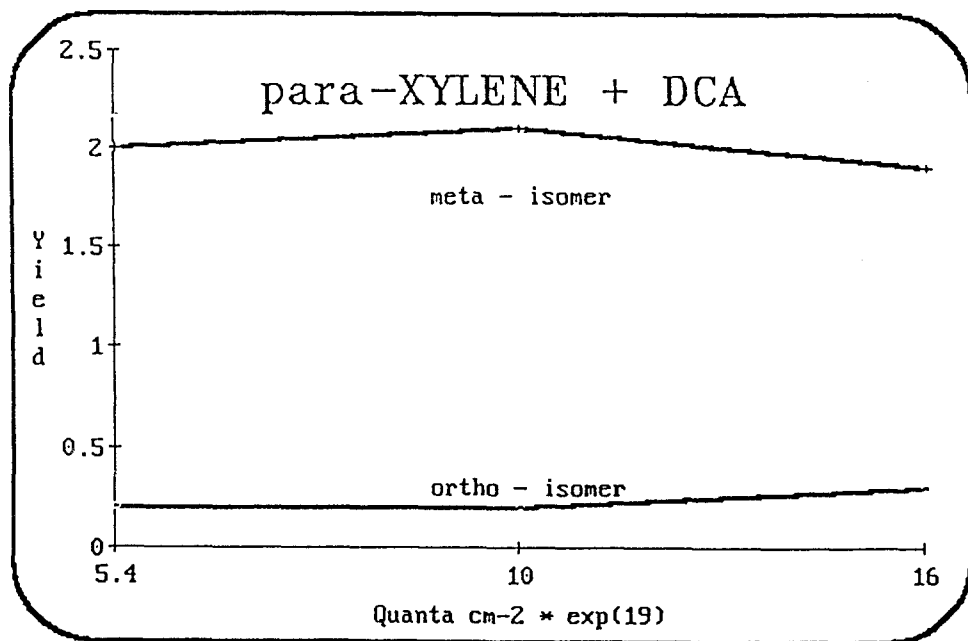


Fig. 6. Yields of products formed during UV irradiation of *p*-xylene in DCA vs. irradiation dose.

Table II. Crystal data: $2C_{24}H_{40}O_4 \cdot C_8H_{10}$, $M = 891.328$

| | A – DCA/ <i>o</i> -xylene | B – DCA/ <i>p</i> -xylene | C – DCA/ <i>m</i> -xylene |
|------------------|---------------------------|---------------------------|---------------------------|
| Space group | $P2_1$ | $P2_1$ | $P2_12_12_1$ |
| <i>a</i> | 7.24 | 7.27 | 7.20 |
| <i>b</i> | 26.17 (unique axis) | 13.38 (unique axis) | 13.69 |
| <i>c</i> | 13.51 | 27.08 | 25.75 |
| β | 90.9 | 91.00 | 90.00 |
| <i>Z</i> | 2 | 2 | 2 |
| Host/guest ratio | 2:1 | 2:1 | 2:1 |

while the third axis is ≈ 7.2 Å (in the α group) or double (≈ 14.2 Å in the β group), or triple (≈ 21.7 Å) [10]. In both α and β groups, the structure of the bilayers is very similar but the relative position of adjacent bilayers is different by a relative shift of ≈ 3.6 Å along the third axis.

Surprisingly the DCA-*o*-xylene and DCA-*p*-xylene complexes belong to the monoclinic system. The DCA-*m*-xylene complex belongs to the orthorhombic system (α group). The two-fold screw axis is parallel to the longest axis in the case of the DCA-*o*-xylene complex and to the intermediate length axis in the case of DCA-*p*-xylene complex. They have cell parameters very close to those of the α group (being $\beta \approx 90^\circ$). In spite of the different space group ($P2_1$) the DCA bilayers and the spatial relationships between bilayers closely resemble those observed in the DCA-*m*-xylene inclusion compound and other DCA complexes exhibiting the $P2_12_12_1$ symmetry (α group).

The similarity is due to the presence of pseudo-two-fold screw axes parallel to both *a* and *c* axes. The spatial relationships between the crystallographic two-fold screw axes and the pseudo-two-fold screw axes parallel to *a* and *c* closely mimic the three non-interesting two-fold screw axes of the $P2_12_12_1$ space group.

It is worthy to note that the pseudo-two-fold screw axes relate to only the DCA molecules and do not repeat the guest molecule which has one definite position.

Figures 7 and 8 show the DCA-*o*-xylene crystal packing and the type of host-guest and guest-guest contacts.

The interatomic distances (3.7–4.2 Å) show that favourable van der Waals' contacts occur between the guest and the host molecules, which stabilize the crystal structure and keep the xylene molecule in a well defined position.

The guest molecules interact very weakly, 4.37 Å being the shortest distance between atoms of two contiguous molecules. The xylene molecules form mono-dimensional crystals and they can be considered almost isolated as the intermolecular contacts are larger than the sum of the vdW radii of the interacting atoms.

The very weak vdW interactions among the *o*-xylene molecules prevent the disproportionation process and allow only the isomerization process.

The three crystal structures are very stable: the intermolecular vdW energy calculated in the range 1–12 Å is about -20 kcal/mol, see Table III.

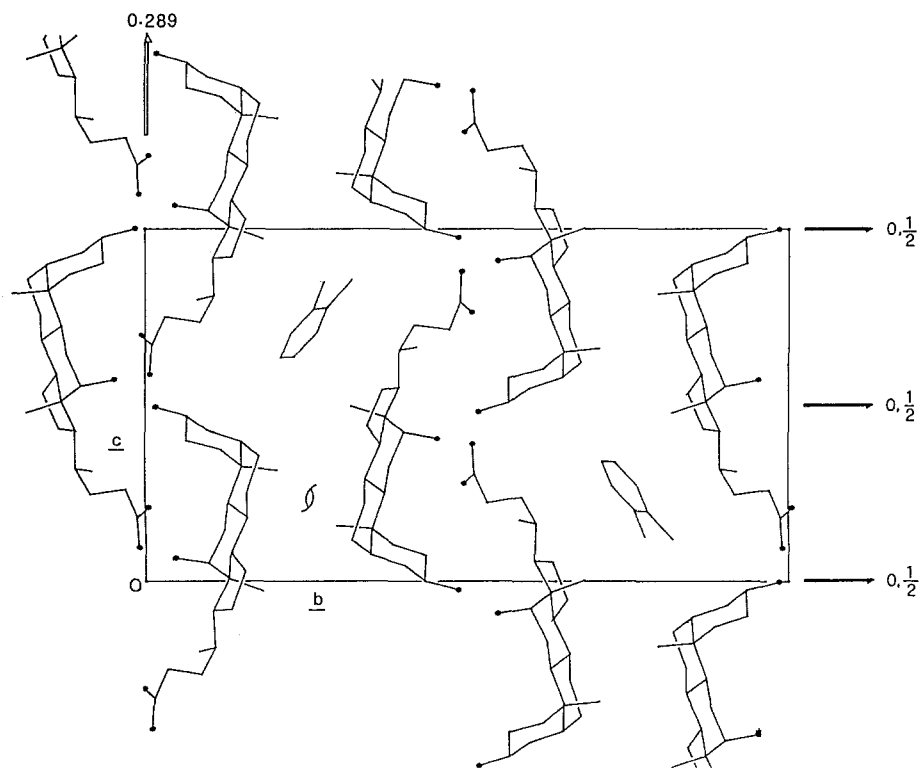


Fig. 7. Arrangement of the host and guest molecules in the DCA *o*-xylene crystal, projected onto the *b*-*c* plane. The crystallographic two-fold screw axes are represented by filled symbols, the pseudo-two-fold screw axes by empty symbols.

Table III. Potential energy calculation (kcal/mol). $V(r) = \{a \cdot \exp(-br)/r^d - cr^{-6}$

| ($\times 10^{-3}$) | <i>a</i> | <i>b</i> | <i>c</i> | <i>d</i> |
|----------------------|----------|----------|----------|----------|
| H—H | 6.6 | 4.080 | 49.2 | 0 |
| H—C | 44.8 | 2.040 | 125.0 | 6 |
| C—C | 301.2 | 0.00 | 327.2 | 12 |
| C—O | 278.7 | 0.00 | 342.3 | 12 |
| O—O | 259.0 | 0.00 | 358.00 | 12 |
| H—O | 42.0 | 2.040 | 132.7 | 6 |

3. Conclusions

The following conclusions may be drawn from these experiments.

(1) The isomerization processes induced photochemically in inclusion compounds are strongly dependent on the molecular host cavities. The main difference compared with the same isomerization processes in solution is the practical elimination of other by-products.

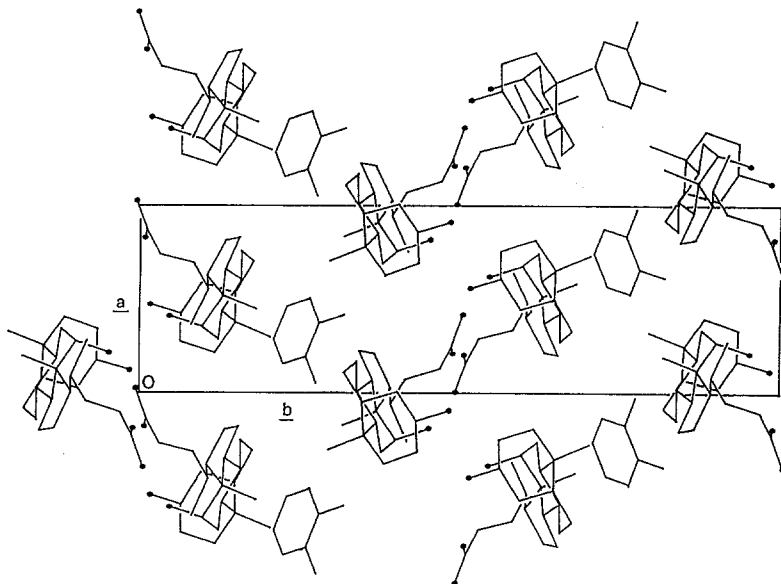


Fig. 8. Arrangement of the host and guest molecules projected onto the a - b plane, showing the monodimensional crystals formed by the o -xylene molecules, sited in between the bilayers of DCA.

(2) The energy transfer process from DCA host molecules to the guest molecules vs. the direct irradiation in an inert solution of hexane shows an overall decrease in the isomerization yields.

(3) The practical consequence is that, in this specific solid state photochemical reaction, there is the advantage of easily guessing the type of reaction product which will be favoured and formed with high purity, and the disadvantage of obtaining this product at lower yield with respect to the solution process; whenever the cost of separation of by-products from the major product is significant, then it seems advantageous to carry out the photochemical process making use of an inclusion compound, which is in any case quite easy to prepare and to dissolve, recovering the product.

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