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Concomitant Photochemical and Phase Rearrangements 2. Luminescent and X-Ray Studies on Photochemistry of Cis- and Trans-1,2-Di-(1 -Naphthyl)ethylenes in the Crystalline State

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Concomitant Photochemical and Phase Rearrangements 2. Luminescent and X-Ray Studies on Photochemistry of Cis- and Trans-1,2-Di-(1-Naphthyl)ethylenes in the Crystalline State

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It is shown that topochemically controlled cis-trans-photoisomerization in crystals of cis-DNE 2–5 μm in size occurs without single crystal destruction. The energy of the newly formed trans-crystal structure is lowered by ca. 5.6 kcal · mole^{-1}. In larger monocrystals the isomerization is accompanied by sample cracking. Photolysis of trans-crystals in the presence of oxygen results in photocyclization and picene formation. The concomitant dimerization and cyclization reactions are not observed in crystalline cis- and trans-DNE which was accounted for by the particular features of the crystal lattice.

I. INTRODUCTION

Photochemical rearrangements in the crystalline state were shown[1] to play an important role in the so-called photophase effect in diarylethylenes. Solid state photochemical reactions are usually controlled either by crystalline structure, or occur on defects and/or on the crystal surface. A remarkable contribution to the topochemistry of these reactions was done by Schmidt and co-workers.[2]

Dimerization of trans-cinnamic acid may be considered as a classic example of topochemical reactions when the crystal structure determines the polymorphic modification of the dimer formed in the photochemical reaction.[3] Photochemical cis-trans-isomerization of cinnamic acid in the crystalline phase has also been thoroughly studied.[4] A large intramolecular rearrangement, the rotation of a fragment at an angle of 180°, is involved in this reaction, and, according to topochemical restrictions[5] and to the principle of rigid molecular stacking,[6] the reaction should be hindered in the crystalline phase. The assumed[4] reaction mechanism involves two stages: the formation of an unstable intermediate dimeric complex followed by isomerization.

The occurrence of photoisomerization in the crystalline diarylethylenes has been reported previously,[7] while the reaction mechanism remained unclear because of the absence of information on the crystalline structure. In the present paper we report some data of luminescent and X-ray studies for cis- and trans-1,2-di-(1-naphthyl)ethylenes (DNE).

2. EXPERIMENTAL

The apparatus for luminescent studies was essentially the same as described elsewhere.[1] Single crystals of cis- and trans-isomers, and/or deposited thin polycrystalline films were used in the experiments. Transparent octahedral single crystals of cis- and yellow planar single crystals of trans were grown from saturated ethanol solutions. Polycrystalline samples 50–100 μm thick were deposited on a cold (77 K) glass support in vacu σ ($5 \cdot 10^{-3}$ torr).

Debye X-ray diffraction diagrams of the powders and polycrystalline films of cis- and trans-DNE were obtained on a diffractometer DRON-1.5.

Crystallographic data for DNE:

	Rhombic cis	Monoclinic trans
a	25.140(7) Å	27.775(13) Å
b	8.124(2)	8.816(8)
c	7.790(2)	6.251(4)
γ	—	84°26′(3′)
Space group	Pbna	*B* 2/*b*
Z	4	4

TABLE I

Atomic coordinates ($\times 10^4$) ($\times 10^3$ for hydrogen atoms) and anisotropic temperature factors of non-hydrogen atoms ($\times 10^4$) (isotropic temperature factors for hydrogen atoms) of cis-DNE ($T_{anisotr} = \exp[-(b_{11}h^2 + b_{22}K^2 + \ldots)]$)

Atom	X	Y	Z	b_{11} (B_j^H)	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C_1	4740(2)	2696(8)	185(6)	15	264	207	−8	−16	28
C_2	4398(2)	3191(6)	1679(7)	16	191	212	8	−11	15
C_3	4587(2)	4242(6)	2884(8)	18	199	243	14	−7	−30
C_4	4254(2)	4772(7)	4228(8)	23	213	267	13	−25	−176
C_5	3745(2)	4199(7)	4373(8)	23	215	226	29	−33	−81
C_6	3543(2)	3048(6)	3173(7)	18	179	170	20	−12	−11
C_7	3016(2)	2469(6)	3287(7)	20	205	216	15	5	−6
C_8	2831(2)	1337(7)	2141(7)	15	229	264	−16	−3	69
C_9	3162(2)	753(6)	814(8)	22	189	262	−3	0	−33
C_{10}	3668(2)	1316(7)	637(8)	15	240	200	−10	4	−55
C_{11}	3880(2)	2482(6)	1825(7)	13	172	204	13	−8	−6
H_1	459(2)	293(6)	−88(7)	5.1					
H_3	498(2)	468(6)	278(6)	3.1					
H_4	442(2)	572(6)	517(6)	3.2					
H_5	346(2)	460(6)	524(7)	4.6					
H_7	276(2)	289(6)	435(6)	3.5					
H_8	243(2)	90(6)	220(6)	3.4					
H_9	301(2)	−20(7)	2(7)	5.6					
H_{10}	393(2)	94(7)	−32(7)	4.3					

TABLE II

Atomic coordinates and anisotropic temperature factors of non-hydrogen atoms of trans-DNE ($\times 10^4$) ($T_{anisotr} = \exp[-(b_{11}h^2 + b_{22}K^2 + \ldots)]$, B_j^H (isotrop.) $= 2$ Å^{-2})

Atom	X	Y	Z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C_1	218(1)	4630(4)	184(7)	13	126	388	2	11	30
C_2	565(1)	4967(4)	1822(7)	12	120	338	−18	−23	24
C_3	411(1)	5834(5)	3558(8)	16	156	428	−17	−14	−41
C_4	724(2)	6172(5)	5161(8)	22	178	474	−23	20	−69
C_5	1206(1)	5673(5)	5077(9)	17	210	370	−22	−26	−1
C_6	1388(1)	4742(5)	3314(8)	14	123	370	−12	12	72
C_7	1886(1)	4163(6)	3170(9)	16	220	591	−22	−72	−52
C_8	2042(1)	3301(6)	1519(10)	12	235	649	−4	−1	−44
C_9	1729(1)	2922(5)	−71(9)	11	305	506	9	24	−99
C_{10}	1256(1)	3489(4)	−11(8)	13	162	441	−7	−16	−139
C_{11}	1066(1)	4384(4)	1678(7)	10	122	331	−7	−26	−6
H_1	301(7)	3626(28)	−750(35)						
H_3	61(7)	6137(25)	3730(38)						
H_4	674(7)	6820(24)	6171(36)						
H_5	1465(7)	5808(25)	6067(38)						
H_7	2090(7)	4461(25)	4283(36)						
H_8	2402(8)	2936(25)	1354(38)						
H_9	1862(7)	2567(25)	−1583(40)						
H_{10}	1068(7)	3045(25)	−1221(38)						

TABLE III

Bond lengths (Å) and angles (°) in cis- and trans-DNE molecules

	cis	trans		cis	trans
$C_1—C_1'$	1.341(6)	1.338(5)	$C_{10}—C_{11}$	1.385(7)	1.392(6)
$C_1—C_2$	1.421(6)	1.457(5)	$C_{11}—C_6$	1.371(6)	1.416(6)
$C_2—C_3$	1.339(7)	1.372(6)	$H_1—C_1$	0.87(5)	1.07(2)
$C_3—C_4$	1.364(7)	1.378(6)	$H_3—C_3$	1.01(5)	0.99(2)
$C_4—C_5$	1.372(7)	1.370(5)	$H_4—C_4$	1.04(4)	0.85(3)
$C_5—C_6$	1.365(7)	1.436(6)	$H_5—C_5$	0.97(5)	0.97(2)
$C_6—C_7$	1.412(6)	1.430(5)	$H_7—C_7$	1.05(4)	0.95(2)
$C_7—C_8$	1.313(7)	1.329(7)	$H_8—C_8$	1.06(4)	1.02(2)
$C_8—C_9$	1.359(7)	1.384(7)	$H_9—C_9$	0.97(5)	1.05(2)
$C_9—C_{10}$	1.364(6)	1.360(4)	$H_{10}—C_{10}$	0.96(5)	1.02(2)
$C_2C_1C_1'$	130.8(4)	124.5(4)	$C_6C_{10}C_{11}$	115.9(4)	117.4(3)
$C_1C_2C_3$	116.0(4)	119.5(3)	$H_1C_1C_1'$	119(3)	118(2)
$C_1C_2C_{11}$	121.4(4)	121.3(4)	$H_1C_1C_2$	110(3)	117(1)
$C_3C_2C_{11}$	122.5(4)	119.2(4)	$H_3C_3C_2$	123(3)	119(2)
$C_2C_3C_4$	117.3(4)	121.8(3)	$H_3C_3C_4$	120(2)	119(2)
$C_3C_4C_5$	121.2(5)	121.3(5)	$H_4C_4C_3$	117(3)	128(2)
$C_4C_5C_6$	122.2(5)	119.5(5)	$H_4C_4C_5$	122(3)	110(3)
$C_5C_6C_7$	122.6(4)	121.8(4)	$H_5C_5C_4$	126(3)	129(3)
$C_5C_6C_{11}$	117.1(4)	119.1(3)	$H_5C_5C_6$	112(3)	110(3)
$C_7C_6C_{11}$	120.2(4)	119.1(4)	$H_7C_7C_6$	116(3)	116(2)
$C_6C_7C_8$	122.2(5)	120.2(5)	$H_7C_7C_8$	122(3)	124(2)
$C_7C_8C_9$	118.4(5)	121.2(4)	$H_8C_8C_7$	124(3)	121(2)
$C_8C_9C_{10}$	121.1(5)	120.0(5)	$H_8C_8C_9$	117(3)	118(2)
$C_9C_{10}C_{11}$	122.2(5)	122.0(4)	$H_9C_9C_8$	117(3)	120(2)
$C_2C_{11}C_{10}$	124.4(5)	123.5(4)	$H_9C_9C_{10}$	121(3)	116(2)
$C_2C_{11}C_6$	119.6(4)	119.1(4)	$H_{10}C_{10}C_9$	122(3)	111(2)
			$H_{10}C_{10}C_{11}$	116(3)	127(2)

Intensities of 504 independent nonzero [$J \geq 1{,}96\sigma$ (J)] reflections in the reflecting sphere up to $(\sin\theta/\lambda) = 0.55$ using Mo K_α radiation and Syntex P1 instrument were measured for 0.3 × 0.3 × 1.0 mm cis-DNE single crystals. No absorption correction has been made. Intensities of 380 nonzero reflections of hk0-hk6 type [$J \geq 2\ \sigma$ (J)] in the reflecting sphere up to $(\sin\theta/\lambda) = 0.55$ using Cu K_α radiation, DAR-UM instrument, and $w - w/2w$ technique were measured for 0.04 × 0.13 × 0.35 mm trans-DNE single crystals. Correction was made for absorption.[8] Structures were solved by a direct method and refined by the full-matrix least square method in an anisotropic (non-hydrogen atoms) and isotropic (hydrogen atoms) approximation with Roentgen-75 program[9] to $R = 0.051$ and $R = 0.045$. Coordinates, bond lengths, and valence angles for cis and trans-DNE are collected in Tables I–III. The energies of the crystalline structure and intermolecular interactions were estimated by the method of atom–atom

6-12 potentials using the program of P. M. Zorky and L. M. Borisanova (Moscow State University).

3. RESULTS AND DISCUSSION

Fluorescence spectra are presented in Figure 1. As is seen, the fluorescence spectra of single crystals and polycrystalline samples of cis-DNE are identical and represent a wide structureless band with a maximum at λ 490 nm, red shifted about 20 nm with respect to the spectra of frozen solutions. The fluorescence spectra of polycrystalline trans-DNE display resolved vibrational structure. A short wavelength band at λ 420 nm was observed for very thin films only.

The fluorescence spectrum of trans-DNE single crystals (as well as that of powders) is remarkably different from the spectrum observed on deposited films, and consists of a wide strong band with $\lambda_{max} = 510$ nm and two weak ones with $\lambda_{max} = 420$ and 440 nm. This redistribution may be due to the reabsorption of the emission from large

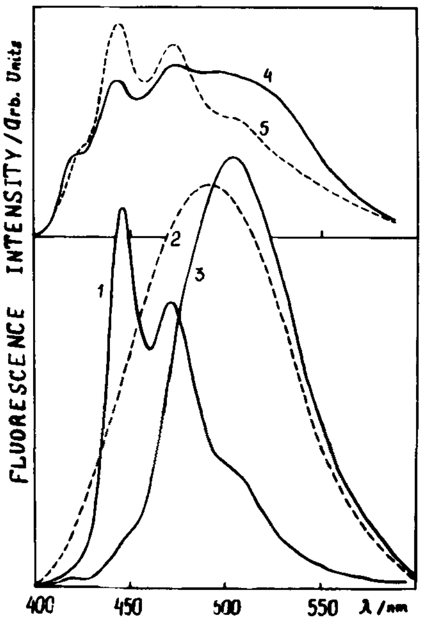


FIGURE 1 Fluorescence spectra of DNE: deposited polycrystalline layer of trans-DNE 1; deposited polycrystalline layer and single crystals of cis-DNE, 2; single crystals and large-crystalline powder of trans-DNE, 3; fluorescence spectrum of deposited layer of cis-DNE after 15 min irradiation, 4; the same after 3.5 h irradiation, 5.

crystals. Deposited films are formed from small crystals, not exceeding several μm, and the reabsorption is negligible.

Upon pulsed excitation from a nitrogen laser, $\lambda_{ex} = 337$ nm, the fluorescence lifetimes, τ, were measured. For deposited samples $\tau = 10^{-9}$ s; for single crystals and powders τ was found to depend upon the emission wavelength, λ_{em}. At λ_{em} of about 420 nm $\tau = 10^{-9}$ s, while at $\lambda\lambda$ near 520 nm $\tau = 2 \cdot 10^{-9}$ s. This is in line with theoretical predictions[10] of the behaviour under reabsorption conditions as well as with experimental data[11] for anthracene crystals.

Polycrystalline and single crystalline samples of cis-DNE were irradiated with filtered emission $\lambda = 366$ nm from a 250 W Hg arc. The irradiation was carried out either in argon atmosphere, or in the presence of atmospheric air. Fluorescence intensity versus irradiation time for polycrystalline films of cis-DNE at $\lambda_{em} = 430$ and 550 nm are given in Figure 2. In argon atmosphere, trans-DNE is formed, and the fluorescence intensity at $\lambda\lambda$ 430–450 nm (corresponding to trans-isomer fluorescence maximum) is increased by as much as a factor of several times. In the course of irradiation the fluorescence spectrum is instantly transformed to the spectrum observed from deposited trans-DNE samples (Figure 1). Upon irradiation of large cis-DNE micro-

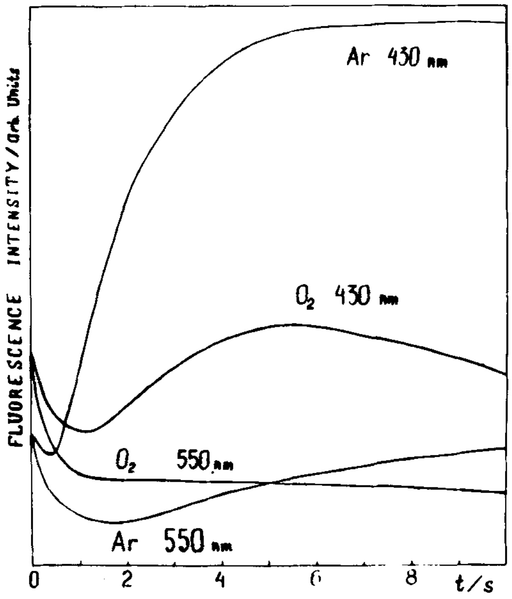


FIGURE 2 Evolution of the fluorescence intensities of polycrystalline layer of cis-DNE at $\lambda = 430$ nm and $\lambda = 550$ nm in atmospheric air and in argon.

crystals, the spectrum of trans-DNE with maximum at $\lambda = 440$ nm, attributed to finely-structured trans-DNE, has also been observed. This may be due to the destruction of large cis-DNE crystals into small pieces of trans-DNE upon irradiation.

In the presence of atmospheric oxygen, picene formation was observed, so that the fluorescence intensity eventually decreased (Figure 2).

X-ray analysis of irradiated cis-DNE single crystals of 0.5 mm in size showed that crystal destruction is spread from the surface into the bulk of the crystal, forming a microcrystalline film on the surface. According to the luminescent data, this film is comprised of trans-DNE molecules. Debye X-ray diagrams from deposited polycrystalline cis-DNE samples of 50–100 μm displayed small number of peaks (Figure 3a). However, these peaks were found to be coincident with those on Debye X-ray diagrams for polycrystalline cis-DNE films prepared by grinding cis-DNE crystals precipitated from solution (Figure 3b). Upon UV irradiation of polycrystalline films of cis-DNE in the absence of O_2, the peak intensities decreased to background level, and some new peaks attributed to the photoproduct appeared (Figure 3c). These peaks were present in the Debye X-ray diagrams for polycrystalline trans-DNE powders precipitated from solutions (Figure 3d). These data enabled the following assumptions to be made:

(i) cis-trans-photoisomerization of DNE is occurring in microcrystalline films of cis-DNE;
(ii) the newly formed photoproduct has a crystalline structure;
(iii) crystal structures of initial cis-DNE and formed trans-DNE are identical to crystal structures of the corresponding isomers precipitated from solution.

Therefore, the data of X-ray analysis provided the essential crystallographic information necessary for elucidating the mechanism of the solid state photoisomerization of DNE.

The molecular structure of cis-DNE is presented in Figure 4. The molecule is non-planar, having crystallographic C_2 symmetry. The planes of naphthyl fragments are turned around $C_1—C_2$ and $C_1'—C_2'$ bonds at an angle of 44.1° in the same direction due to steric hindrances between C_3, H_3 and C_3' and H_3' atoms. Steric hindrances are also responsible for the non-planar configuration of ethylenic fragment around $C_1{=}C_1'$ at an angle of 14.6°.

Intramolecular non-valence contacts $H_3 \ldots H_3'$ and $C_3 \ldots C_3'$ 2.083 Å remain to be shrank[12] even in this molecular structure. Nevertheless, the length of $C_1{=}C_1'$ ethylenic bond 1.341(6) Å is coincident with

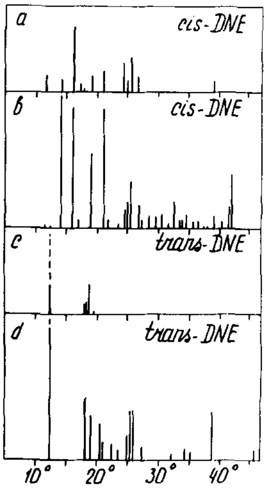


FIGURE 3 Debye X-ray diagrams for deposited polycrystalline layer and polycrystalline powder of cis-DNE (*a* and *b* respectively) and trans-DNE (*c* and *d* respectively).

reported[13] values 1.329–1.337 Å for cis and trans diarylethylenes within the uncertainty limits.

The molecular structure of trans-DNE is given in Figure 5. The molecule has a center of symmetry and is much more planar, sterically unhindered. Naphthyl fragments are turned around C_1—C_2 bond at an angle of 18.3° only, probably, due to intramolecular non-valence repulsions between H_1 and H_{10} atoms, as well as to packing conditions. The bond lengths are consistent with published[13] data for other diarylethylenes, with the exception of C_1—C_2 bond in cis-DNE.

Photochemical cis-trans-isomerization of DNE is accompanied by the lowering of molecular symmetry from rhombic (space group Pbna)

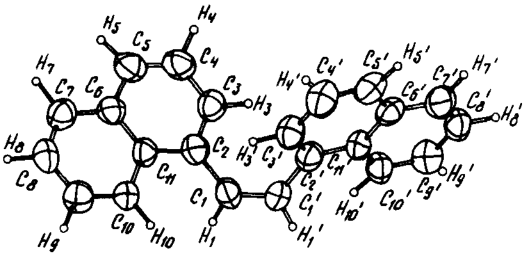


FIGURE 4 The general appearance of cis-DNE molecule at 40% probability of the thermal ellipsoids.

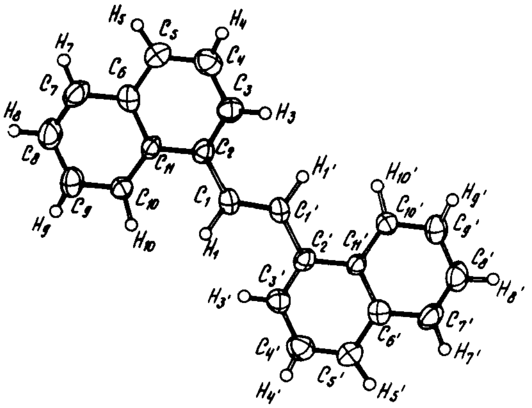


FIGURE 5 The general appearance of trans-DNE molecule at 40% probability of the thermal ellipsoids.

to monoclinic (space group B $2/b$). The cell parameters are changed only slightly (cf. Experimental).

It could be seen from the projection onto the *XOZ* plane (Figures 6, 7), that the stacking motives for cis and trans-molecules in the lattice are similar. The molecules form blocks parallel to the *OYZ* plane, its width being determined by the long molecular axis. The molecules are closely stacked inside these blocks, and the energy of interaction between the nearest neighbours 1.1'; 1.1'' is -9.5 and -6.8 kcal · mole^{-1} in the rhombic modification, and -9.9 and -7.4 kcal · mole^{-1} in the monoclinic. The interaction between the nearest molecules in neighbouring blocks is 1.3–1.8 kcal · mole^{-1}. This may result in an increased block mobility. Upon transition from rhombic cis to monoclinic trans the block symmetry determined by the presence of inversion centers and of rotational double bonds parallel to the "*C*" axis and displaced from the inversion centers by 1/4"*b*", is conserved. In rhombic cis-form, the molecules are situated on double axes and are bound to the nearest neighbours via the inversion center so that ethylenic bonds of neighbour molecules are at the distance C...C'' of 4.07 Å.

In the monoclinic trans-structure, the molecules are at centrosymmetric sites and are bound to neighbours by rotational double bonds. The ethylenic double bonds are at a distance of 4.06 Å. This analogy and genetics in crystal structure imply that cis-trans-isomerization may be assumed to occur in the crystal lattice cage of the cis-isomer. The observed photolytic formation of the trans-isomer in deposited cis-DNE samples strongly supports this point of view. The cis-trans

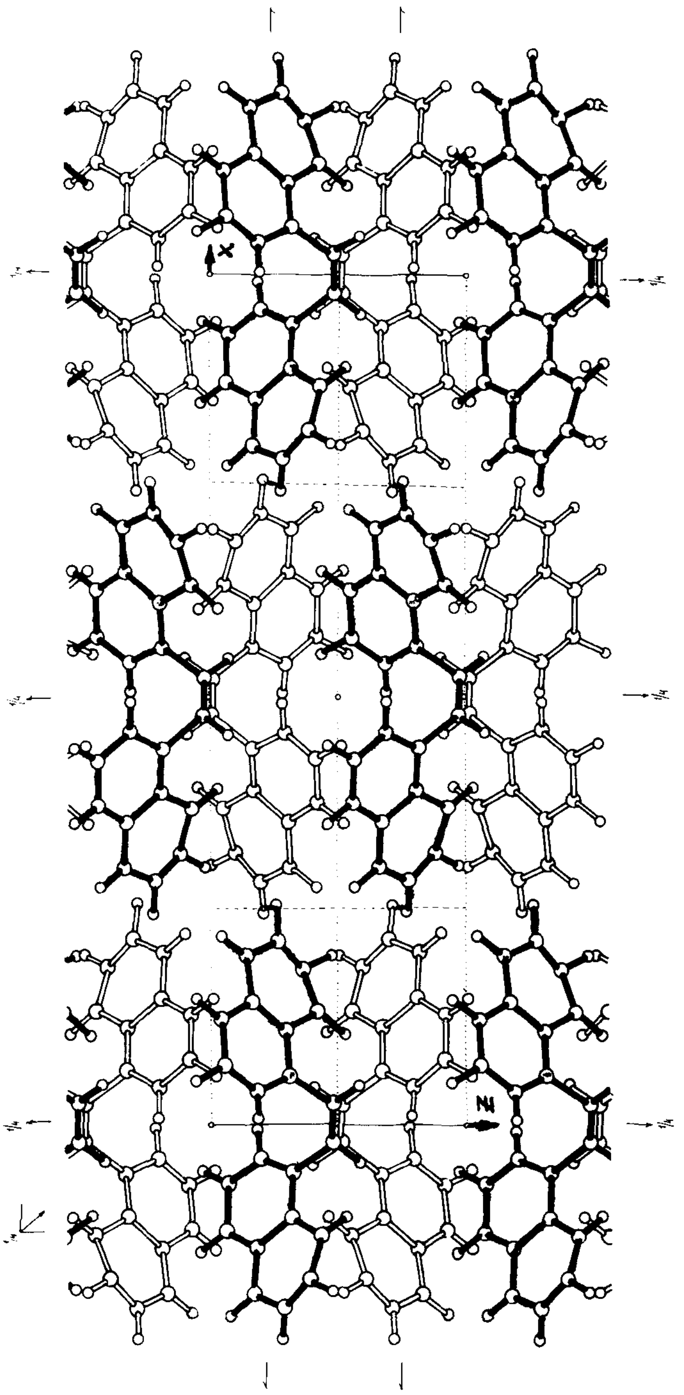


FIGURE 6 Projection of the cis-DNE crystal structure on the *XOZ* plane.

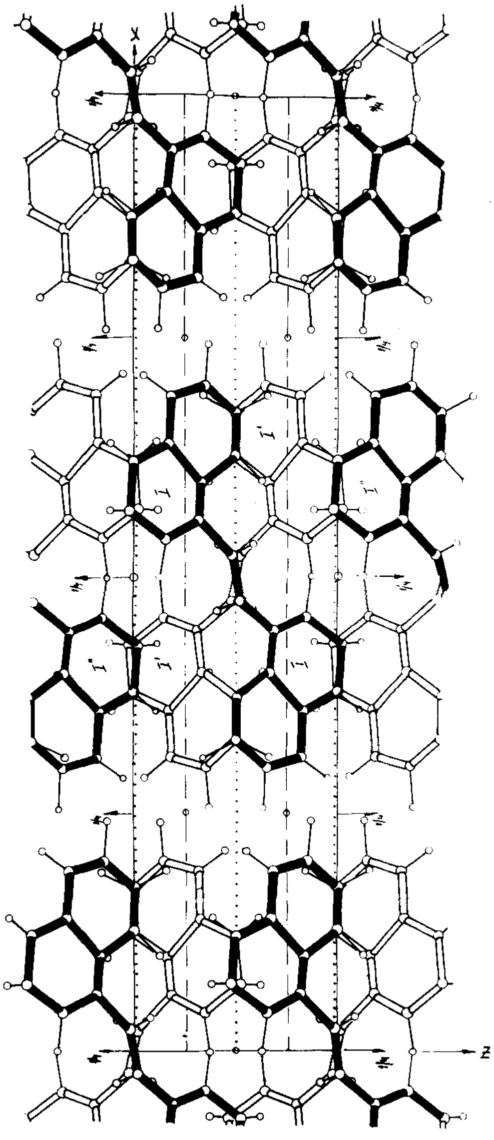


FIGURE 7 Projection of the trans-DNE crystal structure on the *XOZ* plane.

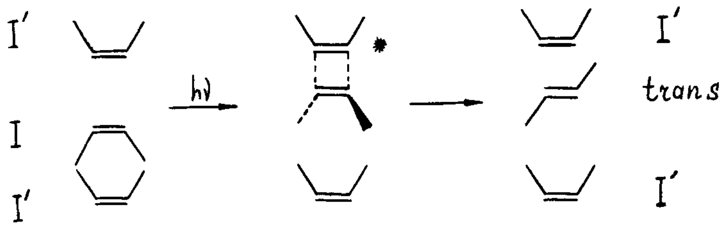
reaction may be thought to occur via spatially chained intermediate "phantom"-isomer 14, accompanied by an increase in non-valence interatomic repulsions between this isomer and nearest 1′ cis-molecule within the block. As a result, the displacement of the excited isomer to the other neighbour molecule 1′ from the opposite side may occur. This displacement is also promoted by the increasing additional interaction between ethylenic carbon atoms of neighbouring molecules. In the excited state, the olefinic π-bond is considerably weakened, and ethylenic carbon atoms thus become more reactive, and the formation of the excited complex between the excited molecule *I* and molecule *I′* may be expected.

The free volume between the excited and unexcited molecules may happen to be sufficient for cis-trans transformation to undergo.

The possibility of complex formation in the cis-trans-isomerization of cinnamic acid was first pointed out by Schmidt,[4] but the detailed mechanism has not yet been discussed so far. The centro-symmetric trans-DNE molecules are bound by rotation symmetry of the second order, parallel to the "*C*" axis, so that block symmetry is conserved in the course of isomerization.

The transition from holohedry $D_{2h} = mmm$ (cis-form) to paramorphous hemihedry $C_{2h} = 2/m$ (trans-form) is accompanied by the loss of vertical symmetry planes in D_{2h} groups and their products on the horizontal plane.[15] That is why in trans-DNE crystals the blocks are bound not by the plane of sliding reflections, but by means of the screw axis parallel to the "*C*" axis. However, the influence of these symmetry elements on the planar molecule nearest to trans-form, is almost equal, and the weak Van-der-Waals interaction forces between blocks induce some mutual displacement.

The transformation of the acoplanar cis-isomer crystal structure into the more planar trans-structure results in the increase in the packing density from 0.706 up to 0.742 and in the decrease in the volume of the monoclinic cell to 1523.4 Å^3 from 1591.0 Å^3. As a result, the density of the trans-DNE crystals is 1.229 g · cm^{-3}, while that of



Scheme I

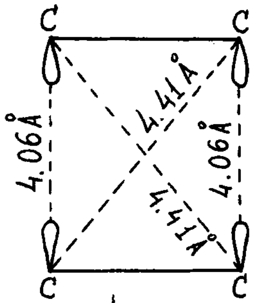
cis-DNE is 1.177 $g \cdot cm^{-3}$. This implies that in the course of the cis-trans-isomerization some free volume should be accumulated along the photoreaction boundary which eventually would result in crystal cracking. Therefore, the cis-trans-isomerization of DNE in crystalline state may be regarded as a topochemically controlled reaction occurring in the crystalline cage of the cis-form. However, the "single crystal-single crystal" transition may occur only within microcrystals. Experiments carried out with microcrystals down to 5 μm in size demonstrated that almost all of the cis-isomer is converted into trans, and the microcrystals remained intact. Some cracks appearing on the crystal surface may however be seen, but we tend to attribute them to the formation of trace amounts of picene in the presence of O_2. Upon irradiation at liquid nitrogen temperatures no destruction was found even at much larger exposures. In crystals of larger size, the cis-trans reaction is accompanied by sample cracking and crystal destruction.

The increase in the packing density in trans-crystals results in the enhancement of the Van-der-Waals interaction in the blocks between the more planar trans-molecules up to -9.9 and -7.4 $kcal \cdot mole^{-1}$ as compared to the acoplanar cis-molecules (-9.5 and -6.8 $kcal \cdot mole^{-1}$). As a result, the energy of the crystal structure of the trans-form is lowered down to -32.1 $kcal \cdot mole^{-1}$ (as compared to -27.7 $kcal \cdot mole^{-1}$ for cis-form), and the stability of the monoclinic trans-structure increases by ca. 5.6 $kcal \cdot mole^{-1}$.

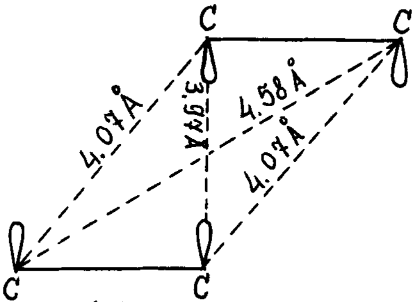
This is probably the reason why, contrary to solutions, the back trans → cis reaction does not occur in crystals. The back polymorphic transitions in crystals are known[16] to occur provided the energy difference between the crystal modifications does not exceed 2–3 $kcal \cdot mole^{-1}$.

The volume of the individual molecules is not significantly changed upon cis-trans-isomerization (281.18 Å^3 for cis and 282.67 Å^3 for trans-molecules). But the volume of the cell occupied by one cis-molecule, 397.8 Å^3, is only slightly larger than that for the trans-molecule, 380.9 Å^3, and is not sufficient for the reaction to occur. Therefore, we tend to believe that the decrease in the trans-cis-isomerization rate at low temperatures (caused by an increased solvent viscosity, as well as in amorphous phase) may be accounted for not by the enlarged molecular volume,[17] but by the energy barrier in the excited state between sterically favourable trans-form and non-planar intermediate states. The energy barrier is absent in sterically hindered but kinetically stable cis-isomer in the π, π^* excited state with minimal π-interaction and weakened π-bond. This implies the independence of the cis → trans conversion of temperature and solvent viscosity.

In the crystalline state cis and trans molecules are stacked in such a manner that ethylenic bonds are situated one over the other thus forming the stacks with the $C_1 \ldots C_1''$ distance of 4.07 Å in the rhombic cis-modification, and of 4.06 Å in the monoclinic trans-modification. According to Schmidt,[3,5] this meets the requirements for "topochemical" dimerization. Ethylenic carbon atoms of neighbouring molecules in the stacks of the trans-isomer form a rectangle, and a rhomb in the cis-isomer stacks.



trans-



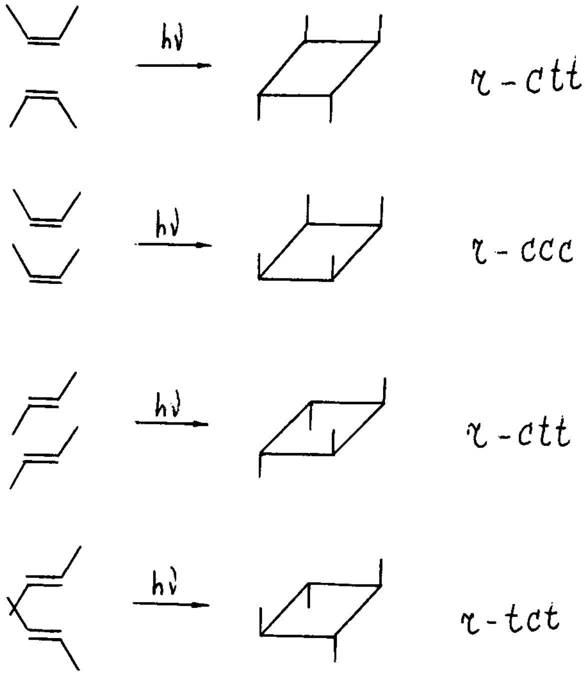
cis-

Therefore, in trans-crystals the situation becomes favourable for consistent suprasurface-suprasurface ($2\pi + 2\pi$) cycloaddition for the photodimerization process.[14,18] In cis-crystals the situation is less convenient for this process. However, experimentally photodimers have not been detected even upon prolonged (over 10 h) irradiation (ca. 10^{20} photons per cm^2) of cis and trans-crystals.

Upon ($2\pi + 2\pi$) photocycloaddition the formation of *r-ctt* and *r-ccc*-dimers in the case of cis-crystals, and *r-ctt* and *r-tct* dimers in the case of tran-crystals becomes possible.[19]

The stacking in cis-crystals favours the formation of *r-ctt* dimers, and that in trans-crystals of *r-tct* dimers.

According to the published data available, mainly trans-DNE are dimerized in the crystalline state giving *r-ctt* dimers, and it is only in solution that traces of *r-tct* dimers were found. The trace amounts of dimers found in cis-crystals are usually related[19] to reaction on imperfections where molecules may have a trans-configuration. Analysis shows that the *r-tct* dimer is somewhat sterically more advantageous as compared to the *r-ctt* dimer. The observed formation of the *r-ctt* dimer may be related to mechanistic features of the photocycloaddition. This may be regarded as a support for the occurrence of the reaction via the excimer between excited and unexcited trans-molecules due to π-interaction between aryl fragments.[14] These excimers could not be formed



Scheme II

in crystals of both isomers, and the dimerization in crystals does not take place, though the topochemical situation is favourable.

The reactions of photodimerization and subsequent polycyclic hydrocarbon formation are known[20] to occur in solutions of cis-diarylethylenes. These reactions do not occur in cis-crystals. The denser packing in blocks with a large energy of intermolecular interactions results in the high conformational rigidity of the cis-molecules and, upon photoexcitation, interferes with their planarization necessary to initiate cyclization. Similar effects were found[21] in studies of photo and thermochromy in crystalline salycylalarylamines.

Photolysis of crystalline cis-DNE results in the formation of crystalline trans-DNE followed by the cyclization (in the presence of O_2) of trans-DNE and picene formation. The picene formation was rather unexpected in structurally unprepared system, and might be rationalized by the formation of some intermediate species, precursor of cycloproduct. It may be assumed that this intermediate is formed by the planar excited cis-isomer formed in the trans → cis reaction held in the matrix of the trans-crystal. The crystal structure of picene, the cyclization product, is known to differ considerably from that of trans-crystal, so that cyclization is accompanied by crystal destruction.

4. CONCLUSIONS

Topochemically controlled cis-trans-photoisomerization in crystals of cis-DNE 2–5 μm in size was found to occur without single crystal destruction. The energy of the newly formed trans-crystal structure is lowered by ca. 5.6 kcal $\cdot$ mole^{-1}, and the back trans-cis reaction becomes energetically unfavourable. In larger monocrystals the isomerization is accompanied by sample cracking. Photolysis of trans-crystals in the presence of oxygen results in photocyclization and picene formation. This reaction leading to the sample cracking is assumed to occur via the formation of the planar cis-isomer in the matrix of the trans-crystal. The concomitant dimerization and cyclization reactions are not observed in crystalline cis and trans-DNE which was accounted for by the particular features of the crystal lattice.

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