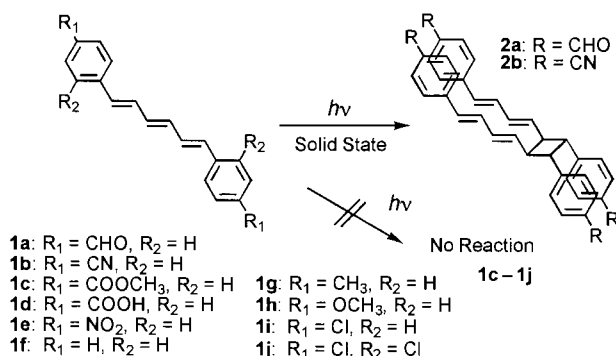# Intermolecular [2+2] Photocycloaddition of Formyl- and Cyano-Substituted Diphenylhexatrienes in the Solid State

Yoriko Sonoda,* Akira Miyazawa, Shigenobu Hayashi, and Masako Sakuragi
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565

Crystalline powder of all-*trans*-1,6-bis(4-R-phenyl)-1,3,5-hexatriene (R = CHO and CN) underwent intermolecular [2+2] photocycloaddition at the 1,2-position of the triene to give mirror symmetric dimers. For the formyl derivative the presence of C–H···O hydrogen bonds was suggested by IR and ^{13}C CP/MAS NMR spectra.

All-*trans*-1,6-diphenyl-1,3,5-hexatriene (all-*trans*-DPH, **1f**) has long been studied mainly because of its unique fluorescence behavior.[1] In spite of numerous reports on the photophysical and photochemical properties of DPH and its derivatives in solution, however, little is known about the photoreactivities in the solid state. Herein, we wish to report the solid-state photoreactions of DPHs having some substituents on the phenyl ring that lead to novel photofunctional materials. Ten kinds of all-*trans*-DPHs (**1a–j**)[2,3] were employed in this study: 1,6-bis(4-R-phenyl)-1,3,5-hexatrienes **1a**: R = CHO, **1b**: R = CN, **1c**: R = COOCH$_3$, **1d**: R = COOH, **1e**: R = NO$_2$, **1f**: R = H, **1g**: R = CH$_3$, **1h**: R = OCH$_3$, **1i**: R = Cl and 1,6-bis(2,4-dichlorophenyl)-1,3,5-hexatriene **1j**. Among them only **1a** and **1b** were photoreactive. They underwent intermolecular [2+2] cycloaddition to give photodimers (and oligomers for the cyano derivative) in the solid state. Although chlorine is a very effective steering group for the solid-state photodimerization of many aromatic molecules including stilbene and 1,4-diphenyl-1,3-butadiene,[4] **1i** and **1j** were photostable as well as the unsubstituted parent compound. The IR and ^{13}C CP/MAS NMR spectra of **1a** suggested the presence of C–H···O hydrogen bonds. The C–H···O type interactions have received considerable attention recently because they are considered to be weak but important forces in organic solids.[5]

1a: R$_1$ = CHO, R$_2$ = H
1b: R$_1$ = CN, R$_2$ = H
1c: R$_1$ = COOCH$_3$, R$_2$ = H   **1g**: R$_1$ = CH$_3$, R$_2$ = H
1d: R$_1$ = COOH, R$_2$ = H   **1h**: R$_1$ = OCH$_3$, R$_2$ = H
1e: R$_1$ = NO$_2$, R$_2$ = H   **1i**: R$_1$ = Cl, R$_2$ = H
1f: R$_1$ = H, R$_2$ = H   **1j**: R$_1$ = Cl, R$_2$ = Cl

On irradiation of crystalline powder of **1a** with a 500-W high-pressure mercury lamp through glass filters ($\lambda > 370$ nm) for 4 h at room temperature in air, mirror symmetric dimer **2a** was obtained as a main product in 16% yield (27% conversion, 58% yield based on the conversion). In contrast to the efficient *trans→cis* isomerization in solution,[6] no isomerization was observed in the solid state.[7]

Compound **2a** was identified from its MS, ^{1}H NMR, IR and UV-vis spectra.[8] The FAB-MS spectrum gave a peak of *m/z* 577 for [M+H]$^+$ corresponding to the dimer. The ^{1}H NMR peaks at δ 4.08 and 3.76 were assigned to the cyclobutane ring protons. The presence of the diene peak at 990 cm^{-1} and the absence of the monoene peak in the region of 960–970 cm^{-1} in the IR spectrum indicated that the compound was formed by the intermolecular cycloaddition at the 1,2-position of the triene. The reaction at the 3,4-position was not observed. This is consistent with the fact that the UV–vis spectrum showed the absorptions of –CH=CH–CH=CH–C$_6$H$_4$–CHO (327 nm) and –C$_6$H$_4$–CHO (260 nm) chromophores. The stereochemistry of the dimer was confirmed by comparison of the coupling patterns of the ^{1}H NMR peaks of the cyclobutane ring protons with those of the mirror symmetric photodimer of 1-(2,6-dichlorophenyl)-4-phenyl-1,3-butadiene.[9,10]

Although the single crystals of high quality for X-ray analysis is not obtained at present, the IR and ^{13}C CP/MAS NMR spectra of **1a** showed the presence of C–H···O hydrogen bonds. The IR peak due to C=O stretching was observed at 1684 cm^{-1} in the solid state, which shifted to lower wavenumber by 14 cm^{-1} as compared to that for the solution in carbon disulfide. The shift can be attributed to the C–H···O=C hydrogen bonds in the solid state. In carbon tetrachloride two peaks were observed at 1700 and 1685 cm^{-1}. The ^{13}C CP/MAS NMR spectrum, on the other hand, gave a peak of carbonyl carbon at 194.5 ppm with a shoulder at 192.5 ppm, while in chloroform-*d* it was observed at 191.5 ppm.[11] For 1,4-benzoquinone which is involved in relatively strong C–H···O interactions, the peak of the carbonyl carbon in the solid state shifts to downfield by 2.4–2.8 ppm from the position in solution.[12] Therefore the shift of 3.0 ppm from 191.5 to 194.5 ppm observed for **1a** is possibly due to the C–H···O hydrogen bonding. The doubling of the peaks at 194.5 and 192.5 ppm may be correlated with the presence of nonequivalence resulting from C–H···O interactions.

The intermolecular interactions in the solid state were also observed in the fluorescence spectra (Figure 1). The spectrum for the diluted solution of **1a** in acetonitrile (AN) was weakly structured with the emission maximum at 468 nm, whereas that in the solid state was broad with the maximum at 568 nm. The red-shifted broad fluorescence in the solid state is probably an emission from an excimer state.

Compound **1b** underwent similar [2+2] photocycloaddition to give mirror symmetric dimer **2b**.[13] Irradiation of **1b** with $\lambda > 370$ nm light for 4 h at room temperature in air gave the dimer in 21% yield (80% conversion, 26% yield based on the conversion). In this case, however, considerable amounts of higher oligomers were isolated by GPC (chloroform eluent) in addition to the dimer. Combination of the IR peaks at 973 (monoene) and 991–993 cm^{-1} (diene) and the MS peak at 230 ((NC–C$_6$H$_4$–CH–)$_2$ fragment) suggested the zig-zag structure of the oligomers as shown below. Thus **1b** showed higher reactivity than **1a**.[14]
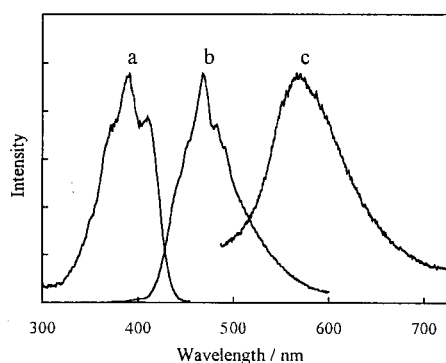
Figure 1. Excitation and fluorescence spectra of **1a**. (a) Excitation and (b) fluorescence spectra in acetonitrile (1×10^{-6} M) and (c) fluorescence spectrum of crystalline powder. Emission wavelength was 470 nm. Excitation wavelengths were (b) 360 and (c) 385 nm.

Fluorescence spectrum of **1b** in the solid state showed a main broad peak at 536 nm, accompanied by a small peak at 469 nm. The main emission maximum moved to longer wavelength by 89 nm compared to that in AN, indicating the presence of some intermolecular interaction in the solid state. In the IR spectrum, however, the position of the peak at 2221 cm^{-1} due to C≡N stretching was the same for the solid state and solution in carbon tetrachloride. The C–H···N≡C hydrogen bonds are therefore considered to be less important than the other stronger forces such as CN···CN dipole-dipole interactions.[15]

A possible structure of the oligomers from **1b**

Ar = 4-cyanophenyl
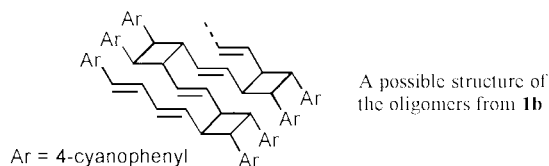
In contrast to **1a** and **1b**, **1c** and **1d** were found to be photostable. For **1c** IR peaks due to C=O stretching were observed at 1720 cm^{-1} in the solid state and 1725 cm^{-1} for the solution in carbon tetrachloride. The small shift of 5 cm^{-1} suggested the weak C–H···O hydrogen bonds, corresponding to the photostability of the compound. For **1d**, on the other hand, the IR peak of C=O stretching was observed at considerably low wavenumber of 1666 cm^{-1} in the solid state, indicating the presence of strong O–H···O hydrogen bonds. The photostability of **1d** may therefore be due to the sheet structure formed by the O–H···O hydrogen bonds, which is unfavorable for the intermolecular [2+2] cycloaddition between the triene double bonds.

As shown above, among the 10 kinds of DPH derivatives studied, only **1a** and **1b** were found to be photoreactive in the solid state. It is noteworthy that the crystal structures of the two photoreactive derivatives are constructed with fairly weak intermolecular interactions.[16]

References and Notes

1   DPH is known to exhibit dual fluorescence from S_1 and S_2: M. T. Allen and D. G. Whitten, *Chem. Rev.*, **89**, 1691 (1989).
2   DPH was purchased from WAKO Pure Chemicals. Other DPH derivatives were prepared according to the modified method described in the literature[3]. **1a**: mp 212–214 °C (recrystallized from AN); **1b**: 223–224 °C (toluene (Tol)); **1c**: 250–251 °C (Tol); **1d**: > 300 °C (No recrystallization solvent was found; products were washed with ethanol and acetone to remove any soluble impurities. The UV–vis and IR spectra of the sample were identical to those reported in the lit-

erature[3]); **1e**: 201–202 °C (Tol); **1f**: 196 °C (1,4-dioxane : ethanol = 2 : 1 (v/v)); **1g**: 206–208 °C (1,4-dioxane : ethanol = 1 : 3 (v/v)); **1h**: 249–250 °C (Tol); **1i**: 217–218 °C (Tol); **1j**: 235 °C (dec) (Tol).
3   C. W. Spangler, R. K. McCoy, A. A. Dembek, L. S. Sapochak, and B. D. Gates, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 151; C. W. Spangler, T. J. Hall, K. O. Havelka, D. W. Polis, L. S. Sapochak, and L. R. Dalton, *Proc. SPIE -Int. Soc. Opt. Eng.*, **1337** (Nonlinear Opt. Prop. Org. Mater. 3), 125 (1990).
4   V. Ramamurthy and K. Venkatesan, *Chem. Rev.*, **87**, 433 (1987).
5   G. R. Desiraju, *Acc. Chem. Res.*, **29**, 441 (1996); G. R. Desiraju, *Chem. Commun.*, **1997**, 1475; S. S. Kuduva, D. C. Craig, A. Nangia, and G. R. Desiraju, *J. Am. Chem. Soc.*, **121**, 1936 (1999).
6   Y. Sonoda, Y. Kawanishi, and M. Sakuragi, *Chem. Lett.*, **1999**, 587.
7   *cis→trans* Isomerization in the solid state seemed to occur for some of the derivatives.
8   **2a**: ^{1}H NMR (CD$_2$Cl$_2$, 600 MHz) δ 9.86 (2H, s), 9.77 (2H, s), 7.72 (4H, d, J = 8.4 Hz), 7.56 (4H, d, J = 8.4 Hz), 7.46 (4H, d, J = 8.4 Hz), 7.13 (4H, d, J = 8.1 Hz), 6.94 (2H, dd, J = 15.6 and 10.4 Hz, –C$_6$H$_4$–CH=CH–), 6.50 (2H, d, J = 15.8 Hz, –C$_6$H$_4$–CH=CH–), 6.33 (2H, dd, J = 15.0 and 10.3 Hz, –C$_6$H$_4$–CH=CH–CH=CH–), 6.21 (2H, ddd, J = 15.2, 5.1 and 2.4 Hz, –C$_6$H$_4$–CH=CH–CH=CH–), 4.08 (2H, dd, J = 3.8 and 2.0 Hz, cyclobutane ring protons adjacent to phenylene) and 3.76 (2H, ddd, J = 7.7, 3.7 and 2.2 Hz, cyclobutane ring protons adjacent to diene); IR (KBr) 3026(w), 2923(m), 2850(w), 2735(w), 1694(s), 1597(s), 1563(m), 1422(w), 1386(m), 1306(m), 1213(s), 1166(s), 1109(w), 1018(w), 990(s), 848(m), 803(m) and 738(m) cm^{-1}; UV–vis λ_{max} (AN) 327 (ε = 4.8 × 10^4 dm^3 mol^{-1} cm^{-1}) and 260 (2.3 × 10^4) nm; FAB-MS m/z 577 [M+H]$^+$; HR-MS m/z Found: 288.1145 (M$^+$/2). Calcd for C$_{20}$H$_{16}$O$_2$: 288.1149; MS (m/z) 288 (100%) (C$_{20}$H$_{16}$O$_2$) and 236 (32%) (C$_{16}$H$_{12}$O$_2$).
9   The solid-state photoproduct from 1-(2,6-dichlorophenyl)-4-phenyl-1,3-butadiene had been identified to be a mirror symmetric dimer.[10] The dimer gave the following data: ^{1}H NMR (CD$_2$Cl$_2$, 600 MHz) δ 7.22 (4H, d, J = 8.1 Hz), 6.99–7.09 (12H, m), 6.60 (2H, ddd, J =16.1, 5.5 and 2.2 Hz, –C$_6$H$_3$–CH=CH–), 6.45 (2H, d, J = 16.5 Hz, –C$_6$H$_3$–CH=CH–), 4.08 (2H, dd, J = 3.9 and 2.0 Hz, cyclobutane ring protons adjacent to phenyl) and 3.84 (2H, ddd, J = 7.3, 3.7 and 2.2 Hz, cyclobutane ring protons adjacent to monoene).
10   M. D. Cohen, A. Elgavi, B. S. Green, Z. Ludmer, and G. M. J. Schmidt, *J. Am. Chem. Soc.*, **94**, 6776 (1972).
11   **1a**: ^{13}C CP/MAS NMR (solid-state, 50 MHz) δ 194.5 (CHO), 192.5 (CHO), 140.9 (arom. C$_4$ (or C$_1$)), 136.1 (arom. C$_1$ (or C$_4$) and triene), 131.1 (triene), 128.9 (arom. C$_2$, C$_6$ (or C$_3$, C$_5$)) and 124.8 (arom. C$_3$, C$_5$ (or C$_2$, C$_6$)); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 191.5 (CHO), 143.1 (arom. C$_4$), 135.3 (arom. C$_1$), 135.0 (triene C$_3$, C$_4$), 132.4 (triene C$_1$, C$_6$) 132.1 (triene C$_2$, C$_5$), 130.2 (arom. C$_3$, C$_5$) and 126.8 (arom. C$_2$, C$_6$).
12   J. R. Scheffer, Y.-F. Wong, A. O. Patil, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, **107**, 4898 (1985).
13   **2b**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.58 (4H, d, J = 8.4 Hz), 7.45 (8H, app. t, J = 7.7 Hz), 7.08 (4H, d, J = 8.4 Hz), 6.90 (2H, dd, J = 15.8 and 10.3 Hz), 6.50 (2H, d, J = 15.8 Hz), 6.34 (2H, dd, J = 15.2 and 10.4 Hz), 6.19 (2H, ddd, J = 15.2, 5.4 and 2.1 Hz), 4.08 (2H, dd, J = 3.6 and 1.8 Hz) and 3.70–3.77 (2H, m); IR (KBr) 3030(w), 2921(m), 2850(w), 2225(s), 1722(w), 1639(w), 1602(s), 1504(s), 1412(m), 1294(w), 1175(m), 1108(w), 1019(w), 990(s), 836(s) and 736(m) cm^{-1}; UV–vis λ_{max} (AN) 309 and 235 nm; HR-MS (m/z) Found: 282.1120 (M$^+$/2). Calcd for C$_{20}$H$_{14}$N$_2$: 282.1155; MS (m/z) 282 (100%) (C$_{20}$H$_{14}$N$_2$), 230 (27%) (C$_{16}$H$_{10}$N$_2$) and 102 (46%) (C$_7$H$_4$N).
14   For **2a** the IR peak of C=O stretching in the solid state shifted to lower wavenumber by only 5–6 cm^{-1} from the position in solution, indicating that the intermolecular C–H···O interactions in **2a** are weaker than those in **1a**. This may be correlated with the inefficient oligomerization for the formyl derivative.
15   The molecules of 4-cyanocinnamic acid are O–H···O hydrogen bonded in the solid state to form centro-symmetrical dimers, which are organized into molecular sheets utilizing CN···CN dipole interactions. The photoproduct is a mirror symmetric dimer: M. S. K. Dhurjati, J. A. R. P. Sarma, and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, **1991**, 1702.
16   Although the presence of C–H···O hydrogen bonds involving aldehyde C=O groups is not clear, 4-formylcinnamic acid forms a photodimerizable β-type crystal: H. Nakanishi, M. Hasegawa, and T. Mori, *Acta Crystallogr., Sect. C*, **41**, 70 (1985).