3066 *J. Phys. Chem. A* **1997,** *101,* 3066−3069

Fluorescence and Photodimerization Studies of Cyano-Substituted Diphenylbutadienes

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Received: September 25, 1996; In Final Form: February 11, 1997[⊗]

Fluorescent emission and photodimerization of crystalline (1*E*,3*E*)-1,4-diphenylbutadiene (**2**, DPB), (1*Z*,3*E*)-1-cyano-1,4-diphenylbutadiene (**3**, CDPB) and (1*Z*, 3*E*)-1-cyano-3-methyl-1,4-diphenylbutadiene (**4**, CMDPB) have been studied. Although crystals of all the three dienes exhibit red-shifted fluorescence, only CDPB (**3**) crystals give [2 + 2] photoproduct on photolysis, despite having a rather long center-to-center distance of 5.04 Å between cyano-substituted double bonds. Large differences in the absorption and fluorescence excitation spectra are observed for crystalline dienes. For example, absorption by a solution of CDPB (**3**) in *n*-hexane is at 339 nm, while its crystals show excitation maximum at 414 nm. However, in solution, the excitation spectra are quite similar. Further, the excitation spectra of crystalline DPB (**2**) and CMDPB (**4**) are much broader and considerably blue shifted relative to that of CDPB (**3**). The difference in the photophysical behavior is related to the crystal structure differences and reactivity differences. The results are discussed in terms of the possible involvement of either excimers or ground state molecular aggregates in the observed photoprocesses.

Introduction

The photoprocesses of α,*ω*-diphenylpolyenes (**1**, DPP, Figure 1) have attracted a great deal of attention in recent years as models of the retinylidene polyenes that are related to vitamin A compounds and retinyl proteins.[1−5] These polyenes exhibit interesting spectroscopic and photochemical properties. Photochemically, these compounds are found to be reactive in solution but are photostable in crystalline state.[6] Solid state [2 + 2] photodimerization reactions of carbon−carbon double bonds of arylalkenes bearing substituent(s) in the aromatic ring have been reported,[7,8] and the excimer state is considered as an intermediate state in the photodimerization process. In the case of crystalline diphenylbutadiene (**2**), it is found that emission and photostability are not intrinsic to the molecule but result from unsuitable packing in the crystal. Diphenylpolyenes containing halo-substituted phenyl group are known to emit from the excimer state and also give [2 + 2] mirror symmetric photoadducts.[6−10] However, no excimer emission from crystalline 1,4-diphenylbutadiene bearing substituent(s) on the linearly conjugated chain carbons has been characterized and reported. Further, there are very few reports in which both photophysical and photochemical observations are made on a solid compound whose structure is well defined.

We report here a study of the fluorescence and photodimerization behavior of crystalline (1*E*,3*E*)-1,4-diphenylbutadiene (**2**, DPB), (1*Z*,3*E*)-1-cyano-1,4-diphenylbutadiene (**3**, CDPB) and (1*Z*,3*E*)-1-cyano, 3-methyl-1,4-diphenylbutadiene (**4**, CMDPB) (Figure 1).

Experimental Section

Compounds **2**−**4**, synthesized as described in the literature,[11,12] gave satisfactory physicochemical data (melting point, IR, and ^{1}H NMR). Photodimerization of crystals coated on a glass plate was effected by irradiating the plate with a 400 W high-pressure Hg lamp. Progress of the photoreaction was monitored by thin layer chromatography (silica gel, 5% ethyl acetate−petroleum ether, 60−80 °C fraction). Fluorescence spectra were recorded on a Spex Fluorolog instrument by exciting the fluorophores at 330 nm (slit width 0.9 nm at excitation and 1.8 nm at emission in front face illumination for the crystalline compounds).

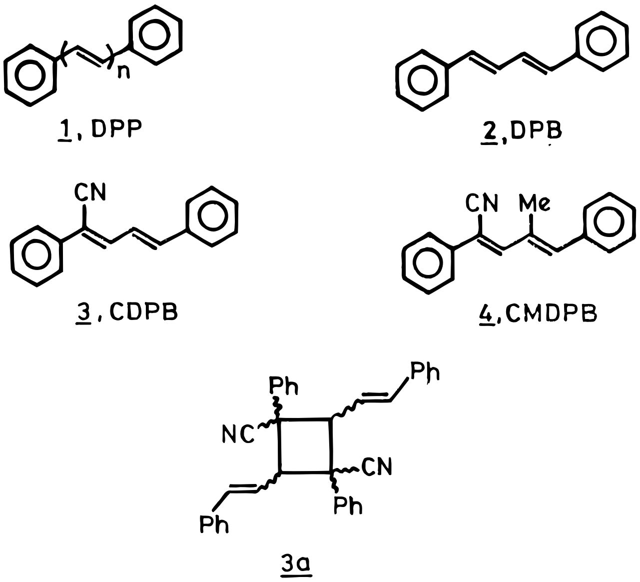

Figure 1. Structures of α,*ω*-diphenylpolyenes (**1**−**4**) and the photodimer **3a**.

Single crystals of compounds were obtained by dissolving the compounds in a minimum quantity of methylene chloride, which was followed by an addition of *n*-hexane from the edges of the conical flask. The flask was sealed and covered with black paper without disturbing the solvent layers and was kept in a refrigerator. The crystals obtained were washed several times with *n*-hexane and dried under vacuum. Crystal parameters for compounds **2** and **4** were obtained and single-crystal data for **3** was solved.

The crystal data are as follows. Compound **3**: $C_{17}H_{13}N_1$, MW 231.3, monoclinic, space group *C*2/*C*, $a = 16.994$, $b = 7.769$, $c = 19.509$ Å, $\beta = 99.63°$, $V = 2593.41$ Å^3, $Z = 8$, $D = 1.21$ mg/m^3, $F(OOO) = 976$, radiation λ (Kα) = 0.7107 Å,

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

S1089-5639(96)02952-0 CCC: $14.00 © 1997 American Chemical Society

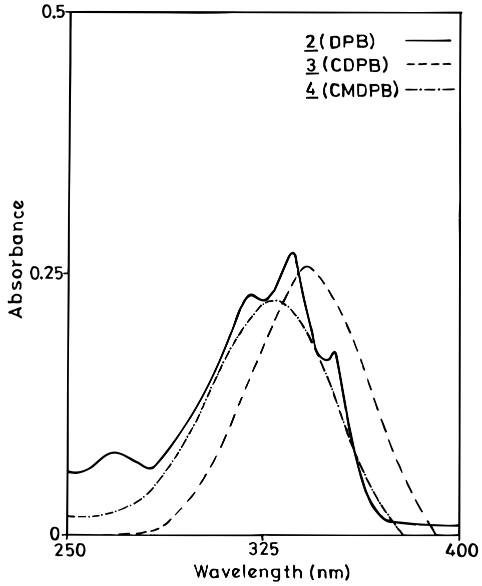

Figure 2. Uv-vis absorption spectra of **2** (—), **3** (— —), and **4** (— • —) in *n*-hexane at 25 °C.

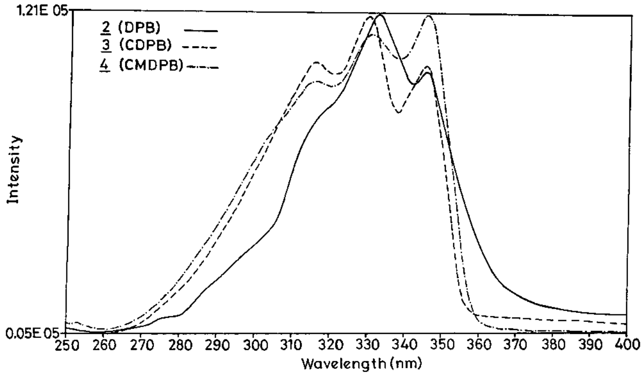

Figure 3. Excitation spectra of **2** (—), **3** (— —), and **4** (— • —) in *n*-hexane at 25 °C.

μ(Mo Kα) = 1.12 mm^{-1}, T = 298 K, 2496 unique reflections. Crystal structure was solved by direct methods and refined using SELX93 (Sheldrick, 1993). In the final cycle refinements, 215 parameters were refined using 1391 observed reflections for which Fo|5σ|Fo, R = 0.57, Rw = 0.057.

Results and Discussion

Uv–vis absorption spectra of dienes **2**–**4** in *n*-hexane are shown in Figure 2. Fluorescence excitation and emission spectra of **2**–**4** in solution in *n*-hexane are presented in Figures 3 and 4, respectively. In Figures 5 and 6, respectively, are depicted fluorescence excitation and emission spectra of crystalline **2**–**4**. Absorption and fluorescence spectral data of compounds **2**–**4** in solution and solid state are summarized in Tables 1, 2, and 3. As evident all the three dienes exhibit red-shifted emission bands in crystalline state as compared to in solution state in *n*-hexane. However, among the three dienes, **3** shows a maximum red shift in its emission.

Irradiation of compound **3** gave a [2 + 2] photoadduct (**3a**). The ^{1}H NMR spectrum (300 MHz, C_6D_6) of the photoadduct **3a** showed multiplet at δ 4.49 due to the protons of cyano-substituted cyclobutane ring. The symmetrical vinylic hydrogens appear as multiplet centered at δ 6.24. A multiplet due to aromatic hydrogens is observed in δ 6.90–7.40 range. Compound **4** did not yield any photoadduct under similar photolytic conditions even after prolonged period of irradiation.

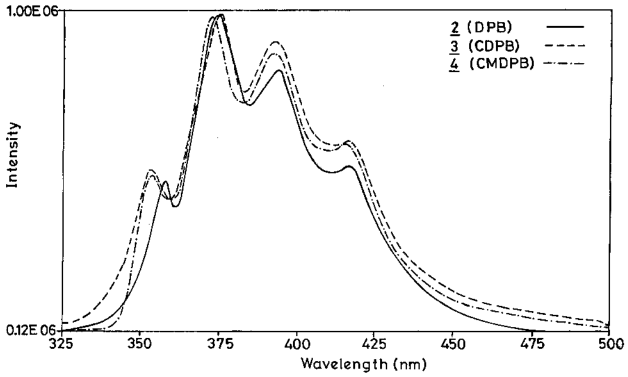

Figure 4. Fluorescence spectra of **2** (—), **3** (— —), and **4** (— • —) in *n*-hexane at 25 °C.

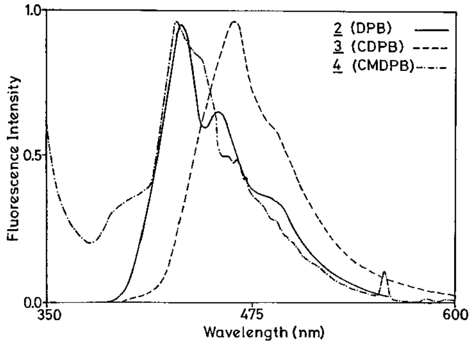

Figure 5. Fluorescence spectra of crystalline **2** (—), **3** (— —), and **4** (— • —) at 25 °C.

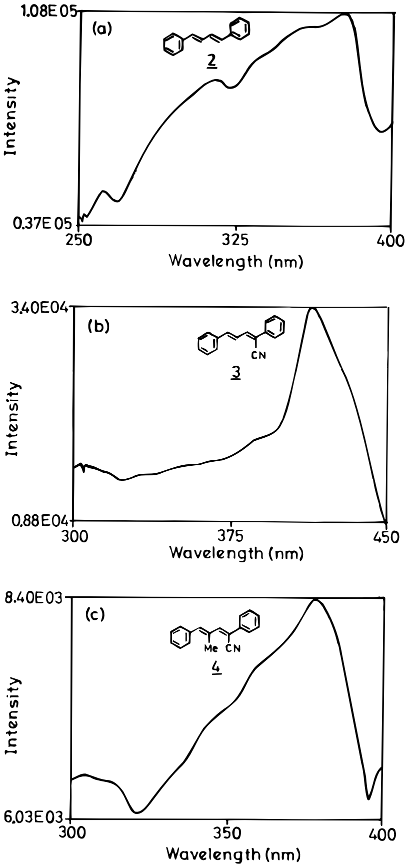

Figure 6. Excitation spectra of crystalline (a) **2**, (b) **3**, and (c) **4** at 25 °C [emission λ_{max} 412 nm].

Cell parameters of compounds **2**, **3**, and **4** are presented in Table 3, and the unit cell crystal packing of **3** is shown in Figure 7. As can be seen, for compounds **2** and **4** one of the cell

TABLE 1: Absorption and Fluorescence λ_{max} of Compounds 2−4 in *n*-Hexane and in Solid State at 25 °C

compound	absorbance λ_{max}	fluorescence λ_{max}		fluorescence shift from solution to solid state
	n-hexane	*n*-hexane	crystal	(cm^{-1})
2	327	375, 395, 418	432	3448
3	339	376, 393, 418	462	5164
4	325	373, 393, 416	428	3446

[a] Excitation for **2**, 330 nm; for **3**, 346 nm; for **4**, 314 nm.

TABLE 2: Excitation Maxima of Compounds 2−4 in *n*-Hexane and in Solid State at 25 °C

compound	excitation max[a] (nm)	
	n-hexane	solid
2	316, 331, 347	376
3	315, 329, 346	414
4	315, 330, 346	379

[a] Excitation spectra recorded employing Spex Fluorolog instrument with emission wavelengths of 375 and 395 nm.

TABLE 3: Fluorescence Emission λ_{max} for Crystalline 2, 3, and 4 at Different Excitation Wavelengths at 25 °C

excitation wavelength (nm)	2	3	4
300	432, 458	462	426
310	432, 458	462	424
320	432, 458	461	427
330	432, 458	461	423
340	432, 457	461	428
350	432, 457	462	422

TABLE 4: Unit Cell Parameters of Crystalline 2, 3, and 4

cell parameters	2	3	4
a	5.89	16.99	6.85
b	7.67	7.76	54.73
c (Å)	53.68	19.5	7.31
α	90.34	90.03	90.01
β (deg)	91.08	99.63	89.99
γ	90.34	89.93	90.02

lengths is too long as compared to that of compound **3**, and compound **3** belongs to a monoclinic space group, whereas compounds **2** and **4** belong to an orthorhombic space group. The phenyl group on C-4 is out-of-plane by 15° (C_{10}-C_{11}-C_{12}-C_{13} dihedral angle). The two phenyl groups are oriented at an 18° angle to each other. The center-to-center distances between two cyano-substituted carbon−carbon double bonds (C_7−C_9) and between the second set of carbon−carbon double bonds (C_{10}−C_{11}) are 5.04 and 4.73 Å, respectively. It may be noted that the molecules of compound **3** are not arranged topochemically in the crystal lattice.

The photostability of **2** in solid state can be explained by considering two topochemical arrangement of the diene. One, in which the central carbon−carbon bonds of two *s-trans*-butadiene molecules overlap, one of which is excited; and the second, wherein both of the double bonds, as well as *s-trans* single bonds, overlapped. An excimer species would be expected for the second topochemical approach.

The [2 + 2] photoadduct observed in compound **3** can be explained in terms of photoinduced dynamic performation concept, where the molecules in the lattice on excitation produce local instability which may lead to large molecular displacement to form an excimer state. From the unit cell packing of compound **3** (Figure 4), it is evident that the molecules are not arranged topochemically and the photoreactive carbon−carbon double bonds are 5.04 Å apart. This observation is a large deviation from the topochemical rules.[7,13−15] To the best of our knowledge, such large distances are not known and a maximum reaction distance of 3.88 Å with double-bond separation distance of 4.83 Å is found in *p*-formyl cinnamic acid.[16,17] As expected, in the photoinduced dynamic performation concept, the molecules of compound **3** need larger displacement to form a [2 + 2] photoadduct.

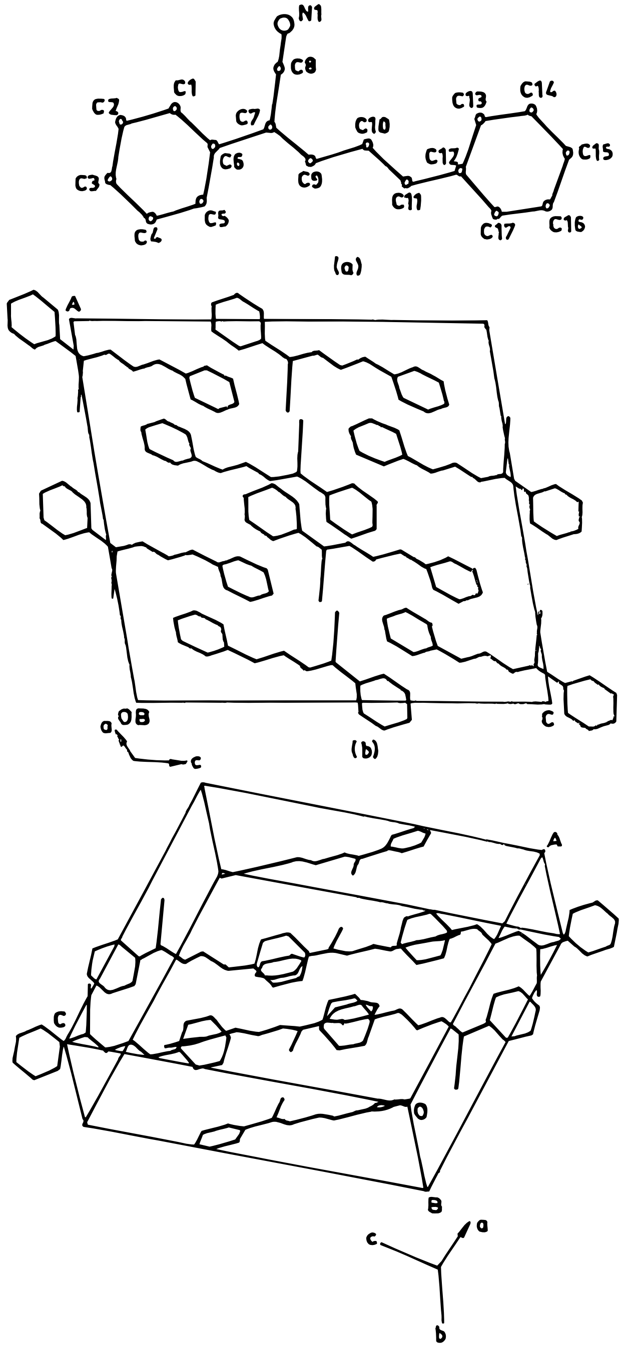

Figure 7. Unit cell crystal packing of **3**: (a) the numbering system used, (b) the crystal packing viewed down axis *b*, (c) the three-dimensional view of unit cell.

The above photochemical and structural results indicate toward the involvement of an excimer in the photoprocesses of cyano-substituted diphenylbutadines. However, the slightly structured pattern of the fluorescent emission band of **3**, a shoulder at around 490 nm, warrants consideration of the observed emission from a monomeric species and possible involvement of ground state aggregates in the emission process. The excitation spectrum of **3** does not show much structured band [Figure 3b] while the excitation spectra of other two dienes, *i.e.* **2** and **4** are characterized by the presence of fine structures in the excitation bands. On the basis of these results, it is quite likely that excimers play role in the photoprocesses of cyano-substituted diene **3**. However, it may be pointed out that the large spectral shifts can be the result of a significant perturbation of the singlet state, probably by exciton splitting.[18] Such may be the case distinctively in dienes **2** and **4** which exhibit reasonably structured emission bands.

A comparison of the absorption spectra in solution state with the excitation spectra in solid state for compounds **2**−**4** reveals that there is a large difference between the absorption and fluorescence excitation spectra for these dienes. For example, absorption maximum of diene **3** is at 339 nm in solution, but the excitation maximum is at 414 nm in solid state. Thus, from solution to solid state there is a drastic shift of 75 nm. However, such a large shift is not seen in the excitation spectra of **3** in solution. Also, the solid state excitation spectra are broader as compared to solution state excitation spectra. These differences in the excitation spectra of **2**, **3**, and **4** suggest that chromophore aggregation is qualitatively different for the unreactive compounds **2** and **4**, relative to the reactive diene **3**. As expected, in solution, the spectra are quite similar (Figure 3), as all the dienes have virtually the same chromophore. The excitation spectra of crystalline **2** and **4** are much broader and considerably blue shifted relative to the spectrum of **3**.

Thus, it is found that, despite having a rather long reaction distance of 5.04 Å, diphenylbutadiene bearing a cyano-substituent on the linear polyene moiety can undergo [2 + 2] photocycloaddition due to their characteristic topographical arrangements in the crystal; wherein the molecules in the lattice on excitation produce local instability which may lead to a large molecular displacement to form an excimer state. Further, crystals of these dienes exhibit photophysical characteristics which are vastly different from their photophysical behavior in solution state, particularly in diene **3**. These differences in the photophysical behavior are related to the crystal structure differences and the reactivity differences.

The present studies bear much significance in photochemical investigations dealing with the effect of chromophore aggregation on photochemistry in organized or partially organized assemblies of crystals, micelles, membranes, polymers, etc.

Acknowledgment. Research grants from the Board of Research in Nuclear Sciences, Department of Atomic Energy, Government of India, are gratefully acknowledged. The authors are thankful to Dr. R. K. Patel, and Dr. V. S. Jakkal for help in X-ray analysis. Thanks are also due to the reviewers of this paper for their valuable suggestions.

Supporting Information Available: Table 1 listing crystal data and structure refinement for **3**, Table 2 listing atomic coordinates and equivalent isotropic displacement parameters for **3**, Table 3 listing bond lengths and angles for **3**, Table 4 listing anisotropic displacement parameters for **3**, and Table 5 listing hydrogen coordinates and isotropic displacement parameters for **3** (8 pages). Ordering information is given on any current masthed page.

References and Notes

(1) Ottolenghi, M. *Adv. Photochem.* **1980**, *12*, 97.

(2) Becker, R. S. *Photochem. Photobiol.* **1988**, *48*, 369.

(3) Birge, R. R. *Biochim. Biophys. Acta* **1990**, *1016*, 293.

(4) Allan, M. T.; Whitten, D. G. *Chem. Rev.* **1989**, *89*, 1691.

(5) Saltiel, J.; Sun, Y.-P. *Photochromism*, Durr, H., Bosa-laurent, H., Eds.; Elsevier: 1990; p 64.

(6) Cohen, M. D.; Elgavi, A.; Green, B. S.; Ludmer, Z.; Schmidt, G. M. J. *J. Am. Chem. Soc.* **1972**, *94*, 6776.

(7) Venkatesan, K.; Ramamurthy, V. *Photochemistry in Constrained and Condensed* Media; Ramamurthy, V., Ed.; VCH: New York, 1991.

(8) For a collection of selected papers by Schimdt, see: Schimdt, G. M. J. *Solid State Photochemistry*; Verlag Chemie: New York, 1976.

(9) Cohen, R.; Ludmer, Z.; Yakhot, V. *Chem. Phys. Lett.* **1975**, *34*, 271.

(10) Warshell, A.; Shakkad, Z. *J. Am. Chem. Soc.* **1975**, *97*, 5679.

(11) Baretz, B. H.; Singh, A. K.; Liu, R. S. H. *Nouv. J. Chim.* **1981**, *5*, 297.

(12) Vogel, A. I. *Text Book of Practical Organic Chemistry*; ELBS: 1978; p 804.

(13) Cohen, M. D.; Schimdt, G. M. J. *J. Chem. Soc.* **1964**, 1996.

(14) Cohen, M. D.; Schimdt, G. M. J.; Sonntag, F. I. *J. Chem. Soc.* **1964**, 2000.

(15) Schimdt, G. M. J. *J. Chem. Soc.* **1964**, 2014.

(16) Nakanishi, F.; Nakanishi, H.; Tsuchiya, M.; Hasegawa, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3096.

(17) Nakanishi, H.; Hasegawa, M.; Mori, T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 70.

(18) Suggested by the reviewer.