Effect of Restricted Mobility of the Linking Chain on Intramolecular Excimer Formation

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Received March 4, 1983

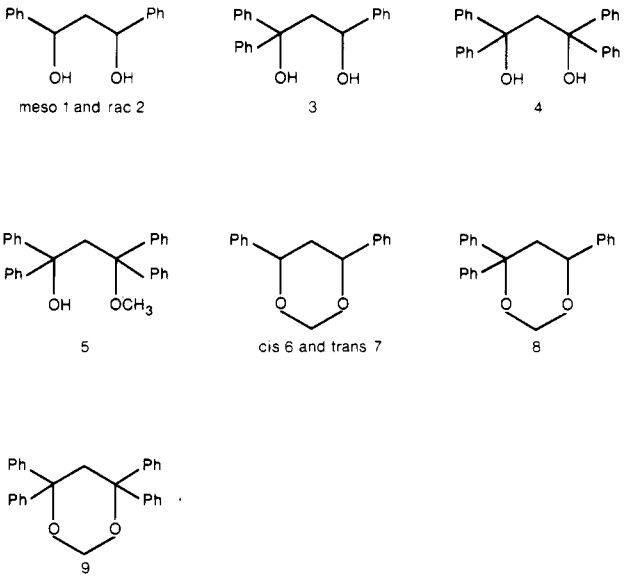
Intramolecular excimer formation in a series of phenyl-substituted 1,3-propanediols, compounds in which the motions of the linking chain are restricted by intramolecular hydrogen bonding, was investigated under stationary conditions in *n*-hexane. The excimer emission properties of these bichromophoric systems were related to the conformational distribution in the ground state obtained from IR studies of the intramolecular hydrogen bonding and compared to the emission characteristics of the corresponding 4,6-polyphenyl-1,3-dioxanes, systems with strongly restricted mobility of the chromophores.

Introduction

Intramolecular excimer formation in bichromophoric systems requires conformational changes in the linking chain, to allow the chromophores to approach each other. The role of the conformational distribution in the ground state has already been discussed for several bichromophoric systems.[1] Recently De Schryver et al.[2] reported the difference in fluorescence properties of *rac*- and *meso*-1,1'-di-(2-naphthyl)diethyl ether as studied by time-resolved measurements. In another contribution[3] the rate constants of excimer formation of *rac*- and *meso*-2,4-diphenylpentane were compared and related to the conformational distribution within each configuration. The observed dual excimer formation in poly(vinylcarbazole) could be elucidated by the study of the excimer fluorescence of the two diastereoisomers of 2,4-di-*N*-carbazolylpentane.[4] A similar idea was worked out by Nishijima et al. for several dinaphthylalkanes.[5]

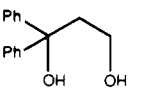
All the above-mentioned systems have one thing in common: the chromophoric groups are linked by a flexible chain. We thought it would be worthwhile to study some systems in which the motion of the linking chain is restricted for instance by intramolecular hydrogen bonding or by ring closure of the linking chain.

In the present contribution the fluorescence properties of *meso*-1,3-diphenyl-1,3-propanediol (**1**), *rac*-1,3-diphenyl-1,3-propanediol (**2**), 1,1,3-triphenyl-1,3-propanediol (**3**), 1,1,3,3-tetraphenyl-1,3-propanediol (**4**), and 1,1,3,3-tetraphenyl-3-methoxypropanol (**5**) obtained by measurements under stationary conditions in *n*-hexane are compared with conformational information obtained by IR measurements of the intramolecular hydrogen bonding. Furthermore the excimer fluorescence of these compounds is compared to that of the corresponding 1,3-dioxanes *cis*-4,6-diphenyl-1,3-dioxane (**6**), *trans*-4,6-diphenyl-1,3-dioxane (**7**), 4,4,6-triphenyl-1,3-dioxane (**8**), and 4,4,6,6-tetraphenyl-1,3-dioxane (**9**).



Results and Discussion

Conformational Analysis from IR Results. Intramolecular OH–OH hydrogen bonding, intramolecular OH–OCH_3 hydrogen bonding, and intramolecular OH–π bonding occur respectively in 1,3-propanediol,[6] 3-methoxypropanol,[7] and ω-phenylalkanols.[8] A study of the IR absorption in the OH stretching region of compound **1** to **5** in dilute CCl_4 solutions ($M \leq 0{,}005$) combined with IR measurements of suitable model compounds, e.g., 1-phenyl-1,3-propanediol[9] and 1,1-diphenyl-1,3-propanediol **10**, will yield conformational information about these



systems (Figure 1). Such kind of analysis was done pre-

(1) (a) L. Bokobza, B. Jasse, and L. Monnerie, *Eur. Polym. J. 13*, 921 (1977); **16**, 715 (1979). (b) Y. Nishijima and M. Yamamoto, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 20*, 391 (1979). (c) H. Morawetz, *Pure Appl. Chem.* **52**, 277 (1980). (d) L. A. Harrah, *J. Chim. Phys. Phys.-Chim. Biol.*, **56**, 383 (1972). (e) C. W. Frank and L. A. Harrah, *Ibid.*, **61**, 1526 (1974).

(2) F. C. De Schryver, K. Demeyer, M. Van der Auweraer, and E. Quanten, *Ann. N. Y. Acad. Sci.*, **93**, 366 (1981).

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(4) F. C. De Schryver, J. Vandendrische, S. Toppet, K. Demeyer, and N. Boens, *Macromolecules*, **15**, 406 (1982).

(5) I. Shinzaburo, M. Yamamoto, and Y. Nishijima, *Bull. Chem. Soc. Jpn.*, **55**, 363 (1982).

(6) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

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(8) (a) P. von R. Schleyer, D. S. Triffan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958). (b) M. Oki and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **32**, 1135 (1959).

(9) N. Mori, S. Omura, and Y. Tsuzuki, *Bull. Chem. Soc. Jpn.*, **38**, 1631 (1965).

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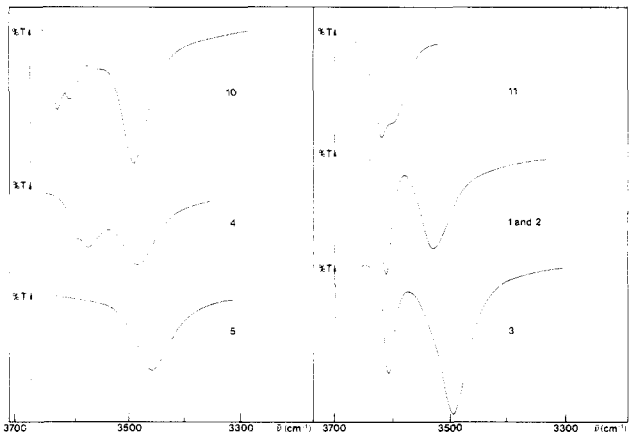
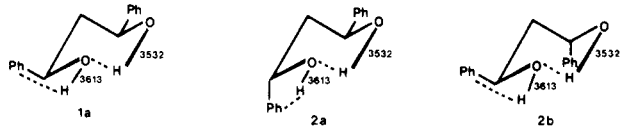


Figure 1. IR spectra of compounds **1–5**, **10**, and **11** in CCl_4 (concentration ≤0.005 M) at room temperature.

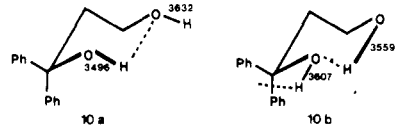
viously by Oki[8b] and by Omura et al.[9] on several monophenylalkanediols.

Both *meso*- and *rac*-1,3-diphenyl-1,3-propanediol (**1** and **2**) show two symmetric bands at 3613 and 3532 cm^{-1}. The former frequency is in accordance with the π–OH bonded ν_{OH} (3615 cm^{-1}) of 1-phenyl-1,3-propanediol[9] and the latter with the secondary OH bonded to the primary OH ν_{OH} (3531 cm^{-1}) of the same compound. As in these two diastereoisomeric compounds, no OH absorption could be detected at 3627 cm^{-1} where 1-phenylethanol[8b] shows a free OH absorption; it can be concluded that *meso*- and *rac*-1,3-diphenyl-1,3-propanediol predominantly exist in conformations **1a**, **2a**, and **2b**.



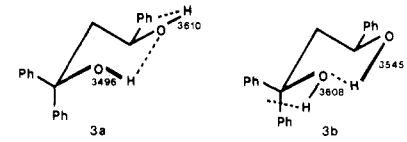
Before discussing the IR results for **3**, **4**, and **5** it is necessary to analyze the OH absorptions of model compound **10**.

The spectrum of 1,1-diphenyl-1,3-propanediol (**10**) can graphically be separated into four symmetric bands at 3632, 3607, 3559, and 3496 cm^{-1}. The bands at 3632, 3607, and 3559 cm^{-1} can be correlated respectively with the free ν_{OH} (3634 cm^{-1}) of 3-phenylpropanol,[8b] the tertiary OH bonded to the π-electrons ν_{OH} (3608 cm^{-1}) of 1,1-diphenylethanol,[10] and the primary OH bonded to the secondary OH ν_{OH} (3547 cm^{-1}) of 1-phenyl-1,3-propanediol.[9] The band at 3496 cm^{-1} can therefore be attributed to the tertiary OH bonded to the primary one. This results in conformations **10a** and **10b** for compound **10**.



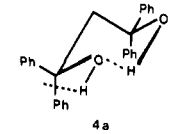
It is interesting to note that the OH to OH hydrogen bond in **10a** is shifted 34 cm^{-1} to lower frequencies with respect to the OH to OH hydrogen bonds in **1** and **2**. This is probably due to the stronger acidity of the tertiary OH group as compared to the secondary one in **1** and **2** because of the effect of the second phenyl group.[11]

1,1,3-Triphenyl-1,3-propanediol (**3**) shows two symmetric bands at 3610 and 3496 cm^{-1}. As is shown in structure **3a**, these bands may be assigned respectively to the secondary

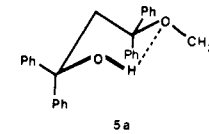


OH bonded to the π-electrons and the tertiary OH bonded to the secondary OH as these values are in agreement with the previously observed ν_{OH} (3613 cm^{-1}) of **1** and **2** and ν_{OH} (3496 cm^{-1}) of **10a**. As no band is observed at 3545 cm^{-1} structure **3b** is, if present, only a minor contributor.

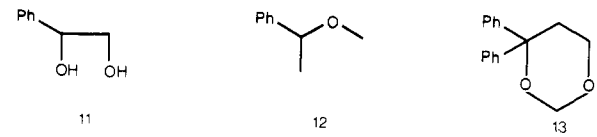
1,1,3,3-Tetraphenyl-1,3-propanediol (**4**) shows a partially resolved doublet with maxima at 3596 and 3574 cm^{-1} and a broad band at 3488 cm^{-1}. The doublet can graphically be separated into two symmetric bands at 3600 and 3574 cm^{-1}. These bands can be assigned to the tertiary OH bonded to the π-electrons. The band at 3488 cm^{-1} is characteristic for the tertiary OH bonded to the tertiary OH and is in agreement with the value of 3496 cm^{-1} observed in structures **3a** and **10a**. From these results it can be concluded that compound **4** exists mainly in conformation **4a**.



1,1,3,3-Tetraphenyl-3-methoxypropanol (**5**) shows a broad band at 3646 cm^{-1}, which may be assigned to the tertiary OH bonded to the methoxy group. The shift of 30 and 24 cm^{-1} to lower frequencies in comparison with the corresponding intramolecular OH to OH hydrogen bonding in **3a** and **4a**, respectively, can be explained by the stronger hydrogen bond, which reflects the higher basicity of the OCH_3 group with respect to the OH group.[12] As no band is present for OH bonded to the π-electrons (3608–3570 cm^{-1}),[13] it can be concluded that compound **5** exists mainly in conformation **5a**.



UV Absorption Spectra. The absorption spectra of compounds **1** to **9** together with the spectra of the model compounds **10**, **11**, **12**, and **13** are shown in Figure 2a–e.



In Figure 2a the absorption spectra of **1** and **2** are compared with that of **11**, while in Figure 2b that of **3** is compared with that of an equimolar mixture of **10** and **11**. Only a slight difference in the vibrational progression of the L_B band is observed. There is however some difference in the vibrational fine structure of **4** and **5** with respect to **10** (Figure 2c) as can be seen in the broadening of the L_B band, accompanied with a slight shift to longer wavelengths. These results can be explained by the conformational information obtained from the IR measurements. This suggests weak interactions between the phenyl groups

(10) M. Oki and H. Iwamura, Bull. *Chem. Soc. Jpn.*, **32**, 950 (1959).
(11) K. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).
(12) A. B. Forster, A. H. Haines, and M. Stacey, *Tetrahedron*, **16**, 177 (1961).
(13) H. Iwamura, *Tetrahedron Lett.*, **26**, 2227 (1970).
(14) D. J. Gram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.* **76**, 6132 (1954).

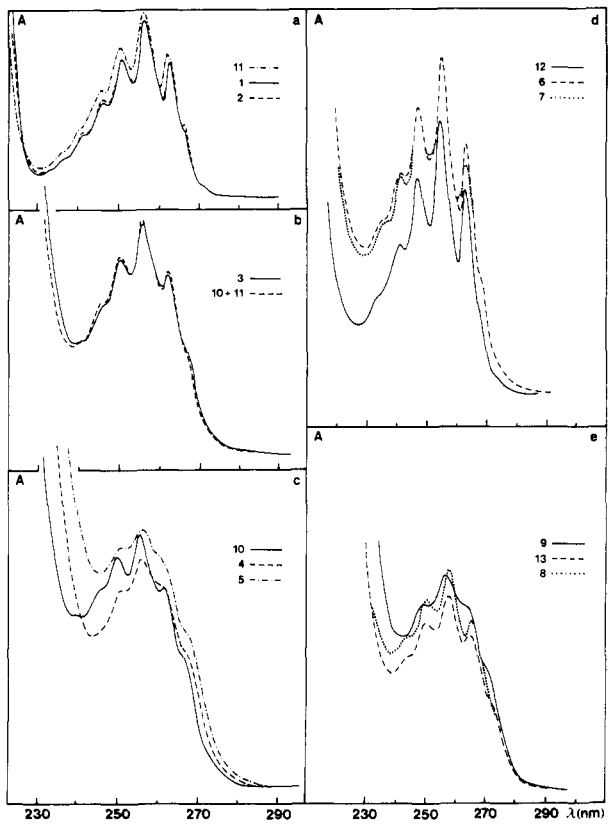


Figure 2. Absorption spectra of **1**, **2**, and **11** (a); **3** and an equimolar mixture of **11** and **10** (b); **4**, **5**, and **10** (c); **6**, **7** and **12** (d); **8**, **9**, and **13** (e) in *n*-hexane at room temperature.

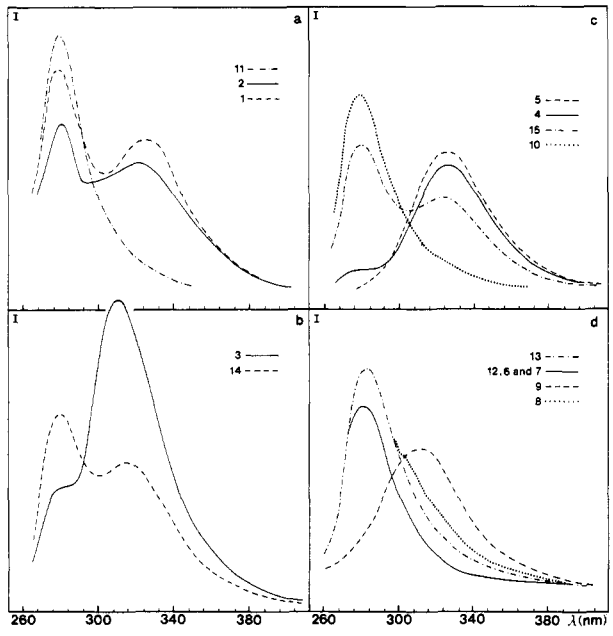


Figure 3. Fluorescence spectra of **1**, **2**, and **11** (a); **3** and **14** (b); **4**, **5**, **10**, and **15** (c); **6–9**, **12**, and **13** (d) in *n*-hexane at room temperature.

in **4a** and **5a** as would be the case in chair distorted or twisted dioxane-like conformations in which the repulsion between the phenyl groups is minimized. The same conclusions can be derived for the dioxane compounds on inspection of the spectral information reported in Figure 2d and 2e.

Fluorescence under Stationary Conditions. The emission spectra of compounds **1** to **13** are reported in Figure 3 together with those of the dimethyl ethers 1,1,3-triphenyl-1,3-dimethoxypropane (**14**) and 1,1,3,3-tetraphenyl-1,3-dimethoxypropane (**15**).

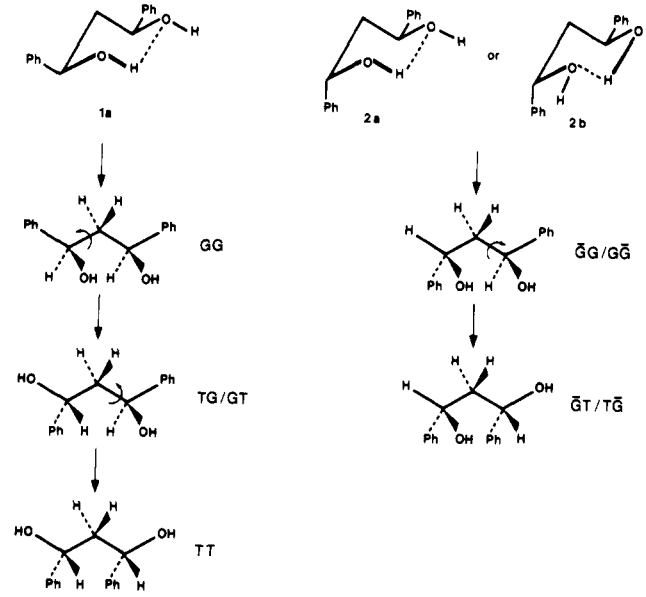


Figure 4. Schematic illustration of excimer formation processes in meso and racemic **1** (a) and **2** (b).

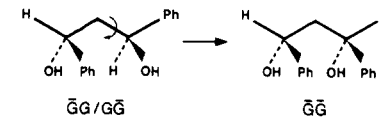


Figure 5. ḠG- and ḠḠ-conformations for *meso*-1,3-diphenyl-1,3-propanediol (**1**).

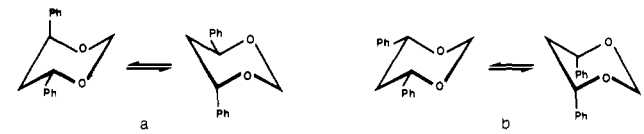


Figure 6. Possible chair conformations in *cis*- and *trans*-4,6-diphenyl-1,3-dioxanes **6** (b) and **7** (a).

The quantum yields of monomer and excimer fluorescence and the ratios and the wavelength of the maximum of excimer emission for the above-mentioned compounds are summarized in Table I.

***meso*- and *rac*-1,3-Diphenyl-1,3-Propanediols (1 and 2).** **1** and **2** show, besides monomer emission at 280 nm, excimer emission at 324 nm (Figure 3a). Contrary to *meso*- and *rac*-2,4-diphenylpentane, where a substantial difference in the excimer emission characteristics is observed (the relative importance of the excimer band is much larger in the meso than in the racemic compound),[1b] **1** and **2** show rather similar emission properties. This can be explained by the conformational transitions that are required in **1** and **2** to reach the excimer state (Figure 4).

As can be seen from Figure 4, in both cases a and b, breaking the intramolecular OH to OH hydrogen bond occurs and only trans to gauche transitions for the phenyl groups or gauche to trans transitions for the hydroxyl groups are required to reach the excimer state. The barrier for these rotations is known to be approximately 15 kJ/mol.[15] In neither case are gauche to gauche rotations, which are probably the reason for the substantially smaller excimer formation rates for *rac*- vs. *meso*-2,4-diphenylpentane[3] and *meso*-2,4-di-β-naphthylpentane,[5] necessary to reach the excimer state.

(15) (a) B. Froelich, C. Noel, B. Jasse, and L. Monnerie, *Chem. Phys. Lett.*, **44**, 159 (1976). (b) D. Y. Yoon, P. J. Flory, and P. R. Sundararayan, *Macromolecules*, **8**, 776 (1975). (c) S. Gorin and L. Monnerie, *J. Chem. Phys. Phys.-Chim. Biol.*, **67**, 869 (1970).

Table I. Quantum Yields of Monomer and Excimer Fluorescence (Φ_{FM}, Φ_{FD}), the Ratio Φ_{FD}/Φ_{FM}, and the Maximum Wavelength of Excimer Emission for Compounds 1 to 15

compd	Φ_{FM}	Φ_{FD}	Φ_{FD}/Φ_{FM}	$\lambda_{max_{excim}}$
1	0.012	0.010	0.86	325
2	0.010	0.012	1.20	324
3	0.012	0.038	3.20	315
4	0.002	0.023	11.50	327
5		0.025		327
6	0.05			
7	0.05			
8	0.04	0.005	0.125	317
9	0.002	0.03	15	325
10	0.040			
11	0.043			
12	0.11			
13	0.044			
14	0.022	0.022	1.00	320
15	0.017	0.020	1.18	327

For **1**, another excimer conformation, the $\bar{G}\bar{G}$ (Figure 5), is possible, but it can only be reached by two subsequent gauche to gauche transitions with respect to the OH groups. This is quite unlikely because of the higher energy barriers for such transitions, which has been reported to be ca. 27 kJ/mol,[16] and because of the steric hindrance between phenyl and hydroxyl groups, which exists in the intermediate $\bar{G}G$ conformation[17] (Figure 5).

***cis*- and *trans*-4,6-Diphenyl-1,3-dioxanes (6 and 7).** For the trans compound no favorable conformation for excimer formation is possible (Figure 6a). In the cis compound, however, such conformation, the diaxial chair, is accessible (Figure 6b). As no excimer fluorescence is observed for **6** (Figure 3d), it can be concluded that (a) the ground state is shifted extremely toward the diequatorial chair; (b) the conversion to the diaxial chair is a slow process as compared to the deactivation processes of the locally excited phenyl chromophore; (c) the activation energy, associated with the chair to chair conversion, must be substantially higher than the barrier for excimer formation in **1** (meso), in which an intramolecular hydrogen bond must be broken.

1,1,3-Triphenyl-1,3-propanediol (3). This compound shows besides monomer fluorescence at 280 nm, excimer fluorescence at 315 nm (Figure 3b). In Figure 7 a scheme for the excimer formation process is shown. As in the case of **2**, breaking the intramolecular hydrogen bond, followed by one trans to gauche rotation of the phenyl group, leads to the excimer state.

While the excimer fluorescence maximum of **3** lies at 315 nm, that of the corresponding dimethyl ether **14** is situated at 320 nm (Figure 3b). As the excimer conformation is the same for both compounds, this difference in the wavelength of the excimer emission could reflect the difference in ground-state enthalpies. This differences is mainly determined by the occurrence of an intramolecular hydrogen bond in **3** which is obviously absent in the dimethyl ether. In energy terms this difference equals 5.9 kJ/mol in favor of the dimethyl ether, which is fairly well in agreement with the value of 4 kJ/mol for the intramolecular hydrogen bond in 1,3-butanediol, obtained by Fishman et al.[18]

4,4,6-Triphenyl-1,3-dioxane (8). The triphenyldioxane **8** exhibits a fluorescence spectrum (Figure 3d) that consists

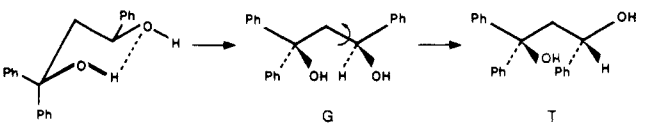
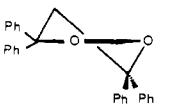


Figure 7. Schematic presentation of the excimer formation process in 1,1,3-triphenyl-1,3-propanediol (**3**).

Figure 8. Chair conformations of 4,4,6-triphenyl-1,3-dioxane (**8**).

mainly of a strong monomer fluorescence at 280 nm with a shoulder at the longer wavelength side. Subtraction of the fluorescence spectrum of **13**, after normalization at 280 nm, yields a structureless emission with a maximum at 317 nm which can be attributed to an excimer. This fluorescence probably originates from the diaxial chair conformation (Figure 8), which is already present at the time of excitation.

1,1,3,3-Tetraphenyl-1,3-propanediol (4), 1,1,3,3-Tetraphenyl-3-methoxypropanol (5), and 4,4,6,6-Tetraphenyl-1,3-dioxane (9). The tetraphenyl diol **4**, the corresponding monomethyl ether **5**, and the tetraphenyldioxane **9** show analogous fluorescence properties (Figure 3c,d). They show, besides little or no monomer fluorescence at 280 nm, a broad structureless excimer band with maxima at 327 nm for the acyclic compounds and at 315 nm for the dioxane. This fluorescence behavior can easily be understood in view of the conformational distribution in the ground state. The acyclic compounds **4** and **5** exist mainly in the hydrogen-bonded conformations **4a** and **5a**, while for the dioxane **9** a nonchair conformation **9a** is most



9a

likely.[19] Even when **4a** and **5a** would be chair distorted or twisted dioxane-like conformations as is suggested by the UV absorption spectra, these conformations are still favorable for fast excimer formation. In any case only minor conformational changes are required to reach the excimer configuration.

It is particularly interesting to note that in compounds **4** and **5**, contrary to the diols **1**, **2**, and **3**, no breaking of the intramolecular hydrogen bond is necessary to reach the excimer configuration. This explains why the maxima of excimer emission for **4** and **5** are nearly identical with that in the corresponding dimethyl ether **15** (Figure 3c).

Conclusion

Our results show that using a six-membered ring as a link between two chromophores is too severe a restriction on the mobility within the lifetime of the phenyl excited state. No chair to chair conversion was observed within the lifetime of the excited state in a series of phenyl-substituted dioxanes. This means that only those dioxane derivatives which have a favorable conformation within their conformational distribution in the ground state can exhibit excimer fluorescence.

In the *cis*-diphenyldioxane such conformations are present in too small an amount, while in the triphenyl

(16) J. E. Piercy and M. G. S. Rao, *J. Chem. Phys. Phys.-Chim. Biol.*, **46**, 3951 (1967).
(17) T. Moritani and Y. Fujiwara, J. Chem. Phys. *Phys.-Chim. Biol.*, **59**, 1175 (1973).
(18) E. Fishman and Tun Li Chen, *Spectrochim. Acta, Part A*, **25 A**, 1231 (1969).
(19) J. E. Anderson, F. G. Riddell, and M. J. T. Robinson, *Tetrahedon Lett.*, 2017 (1967).

compound the conformational distribution in the ground state is such that at least a fraction of the molecules have two phenyl chromophores in the diaxial position. In the tetraphenyldioxane the conformation is always favorable for excimer formation, although it is very likely that the ground state has a nonchair conformation.

By inducing less restriction on the mobility of the linking chain, using hydrogen bonding, we obtained a system with enough flexibility for intramolecular excimer formation but which allowed conformational analysis. From IR data the conformational distribution in the ground state was obtained and related to the amount of excimer emission.

As the conformational distribution in 1,3-diphenyl-1,3-propanediol is changed appreciably with respect to that in 2,4-diphenylpentane, because of hydrogen bonding, the difference between the diastereoisomers is much less pronounced in the diols.

Experimental Section

Absorption spectra were recorded on a Perkin-Elmer 124 double-beam spectrophotometer. Optical densities were measured with a Varian or a Hitachi spectrophotometer. Corrected emission spectra were run on a "Fica absolute and differential fluorometer". The concentration of the compounds was 10^{-4} M. All samples were degassed by at least four freeze–thaw cycles. *n*-Hexane was purchased from Merck (Uvasol) and used without further purification. Fluorescence quantum yields were determined (at 25 °C) by comparing the integrated spectrum of a sample with that of a solution of quinine sulfate in 1.0 N H_2SO_4 having the same optical density at the excitation wavelength. IR spectra were recorded on a Perkin-Elmer double-beam ratio-recording spectrophotometer. The ^1H NMR spectra have been taken on a Varian 60-MHz, a Varian XL-100, a Varian 300-MHz, or on a Brucker 360-MHz spectrometer. ^{13}C NMR spectra were run on a Varian XL-100 instrument.

1,3-Diphenyl-1,3-propanediols (1 and 2). The diols **1** and **2** were prepared by hydrogenation under pressure (2 atm) of 1,3-diphenyl-1,3-propanedione (commercially available from Aldrich) with a Raney nickel catalyst. A first purification was performed by column chromatography on alumina with CH_2Cl_2/CH_3CN (80/20), which resulted in a 50/50 mixture of **1** and **2**; yield 80%. Separation of **1** from **2** was obtained by preparative HPLC on alumina with hexane/CH_2Cl_2/MeOH (79/20/1). Both **1** and **2** were recrystallized from CH_2Cl_2/pentane (50/50), which resulted in white crystals with mp 104–105 °C and 125–126 °C, respectively.

1: ^1H NMR ($CDCl_3$, 360 MHz) δ 1.96 (1, ddd, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −14.5 Hz, $J_{H_{2a}H_{2b}}$ = 2.5 Hz $J_{H_{2a}H_3}$ = 2.5 Hz), 2.23 (1, ddd, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −14.5 Hz, $J_{H_{2b}H_1}$ = 10 Hz, $J_{H_{2b}H_3}$ = 10 Hz), 3.25 (2, s, OH), 5.05 (1, dd, 1-CH, $J_{H_1H_{2a}}$ = 2.5 Hz, $J_{H_1H_{2a}}$ = 2.5 Hz, $J_{H_1H_{2b}}$ = 10 Hz), 5.05 (1, dd, 3-CH, $J_{H_3H_{2a}}$ = 2.5 Hz, $J_{H_3H_{2b}}$ = 10 Hz), 7.30 (10, m, aryl H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.95; H, 7.01. Found: C, 78.85; H, 6.96.

2: ^1H NMR ($CDCl_3$, 360 MHz) δ 2.18 (1, ddd, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −15 Hz, $J_{H_{2a}H_1}$ = 5.5 Hz, $J_{H_{2a}H_3}$ = 6.5 Hz), 2.18 (1, ddd, 2-CH_aH_b, $J_{H_{2b}H_{2a}}$ = −15 Hz, $J_{H_{2b}H_1}$ = 6.5 Hz, $J_{H_{2b}H_3}$ = 5.5 Hz), 2.85 (2, d, OH, J = 2.5 Hz), 5.00 (1, ddd, 1-CH, $J_{H_1H_{2a}}$ = 5.5 Hz, $J_{H_1H_{2b}}$ = 6.5 Hz, $J_{H_1,10H}$ = 2.5 Hz), 5.00 (1, ddd, 3-OH, $J_{H_3H_{2a}}$ = 6.5 Hz, $J_{H_3H_{2b}}$ = 5.5 Hz, $J_{H_3,3OH}$ = 2.5 Hz), 7.30 (10, m, aryl H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.95; H, 7.01. Found: C, 78.87; H, 6.94.

1,1,3-Triphenyl-1,3-propanediol (3). Diol **3** was prepared by refluxing a three-fold excess of PhMgBr with ethyl 3-hydroxy-3-phenylpropionate[20] in diethyl ether for 4 h. The reaction mixture was poured into a 10% solution of NH_4Cl in H_2O and extracted with CH_2Cl_2. The purification of **3** was performed by column chromatography on alumina with CH_2Cl_2, followed by recrystallization from pentane/CH_2Cl_2 (70/30), which resulted in colorless crystals: mp 127–128 °C; yield 30%; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.68 (1, dd, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −15 Hz, $J_{H_{2a}H_3}$ = 9.5 Hz), 2.68 (1, ddd, 2-CH_aH_b, $J_{H_{2b}H_{2a}}$ = −15 Hz, $J_{H_{2b}H_3}$ = 3 Hz, $J_{H_{2b},3OH}$ = 1 Hz), 2.90 (1, dd, 3-OH, $J_{H_3,3OH}$ = 2.5 Hz, $J_{H_{2b}3OH}$ = 1 Hz), 4.70 (1, s, 1-OH), 4.72 (1, ddd, 3-CH, $J_{H_3H_{2a}}$ = 9.5 Hz, $J_{H_3H_{2b}}$ = 3.0 Hz, $J_{H_3H_{2b}}$ = 3.0 Hz, $J_{H_3,3OH}$ = 2.5 Hz), 7.30 (15, m, aryl H). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.89; H, 6.58. Found: C, 82.65; H, 6.54.

1,1,3,3-Tetraphenyl-1,3-propanediol (4). Diol **4** was prepared by refluxing a threefold excess of PhMgBr with ethyl 3-hydroxy-3,3-diphenylpropionate[22] in diethyl ether during 6 h. The reaction mixture was poured into a 10% solution of NH_4SO_4 and extracted with diethyl ether. A first purification was performed by crystallization from hexane/petroleum ether (50/50). Further purification was obtained by column chromatography on alumina with CH_2Cl_2, followed by recrystallization from CH_2Cl_2/pentane (10/90), which resulted in white needles: mp 112–113 °C; yield, 22%; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.52 (2, s, CH_2), 4.10 (2, s, OH), 7.40 (20, m, aryl H). Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.26; H, 6.32. Found: C, 84.93; H, 6.31.

1,1-Diphenyl-1,3-propanediol (10). Diol **10** was prepared by Grignard reaction of a twofold excess of PhMgBr with propiolactone in diethyl ether during 5 h at room temperature. The reaction mixture was poured into a 10% solution of NH_4Cl in H_2O and extracted with CH_2Cl_2. Purification by column chromatography on alumina with CH_2Cl_2/CH_3CN (70/30), followed by recrystallization from CH_2Cl_2/pentane (60/40), yielded white needles: mp 90–91 °C; yield, 40%; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.45 (1, s, 3-OH), 2.55 (2, t, 2-CH_2, $J_{H_3H_2}$ = 5 Hz), 3.75 (2, t, 3-CH_2, $J_{H_3H_2}$ = 5 Hz), 4.10 (1, s, 1-OH), 7.30 (10, m, aryl H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.95; H, 7.02. Found: C, 79.21; H, 7.09.

4,6-Diphenyl-1,3-dioxanes (6 and 7). Dioxanes **6** and **7** were prepared by acid acetalization of 1,3-diphenyl-1,3-propanediol with formaldehyde. A first purification was performed by column chromatography on silica with CH_2Cl_2, which yielded a 45/55 mixture of **6** and **7**; yield 60%. Separation of **6** from **7** was obtained by HPLC on silica with CH_2Cl_2/CH_3CN (98.8/1.2). Both **6** and **7** were recrystallized from petroleum ether, which afforeded white crystals with mp 242–243 °C and 100–101 °C respectively. *cis*-**6**: ^1H NMR ($CDCl_3$, 100 MHz) δ 1.90 (2, m, 5-CH_2), 4.62 (2, m, −CHPh), 4.87 (1, d, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −6.4 Hz), 7.40 (10, m, aryl H); ^{13}C NMR ($CDCl_3$) δ 41.73 (C-5), 79.01 (C-4 and C-6), 94.32 (C-2). Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.66. Found: C, 79.89; H, 6.62. *trans*-**7**: ^1H NMR ($CDCl_3$, 300 MHz) δ 2.48 (2, t, 5-CH_2, J = 5.5 Hz), 5.00 (2, t, −CHPh, J = 5.5 Hz), 5.02 (2, s, 2-CH_2), 7.35 (10, m, aryl H); ^{13}C NMR ($CDCl_3$) δ 35.17 (C-5), 73.61 (C-4 and C-6), 89.03 (C-2). Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.66. Found: C, 80.09; H, 6.71.

4,4,6-Triphenyl-1,3-dioxane (8). Dioxane **8** was prepared by a Williamson ether synthesis, in which the disodium alkoxide of the corresponding diol **3** was allowed to react with CH_2Br_2 in THF for 8 h at room temperature. Purification was performed by column chromatography on silica with benzene/CH_2Cl_2 (80/20), followed by recrystallization from petroleum ether, which resulted in white crystals: mp 81–82 °C; yield 40%; ^1H NMR ($CDCl_3$, 100 MHz) δ 2.24 (1, dd, 5-CH_aH_b, $J_{H_{5a}H_{5b}}$ = −14.1 Hz, $J_{H_{5a}H_6}$ = 11.6 Hz), 2.90 (1, dd, 5-CH_aH_b, $J_{H_{5a}H_{5b}}$ = −14.1 Hz, $J_{H_{5b}H_6}$ = 2.4 Hz), 4.83 (1, dd, 6-CHPh, $J_{H_6H_{5b}}$ = 2.4 Hz, $J_{H_6H_{5a}}$ = 11.6 Hz), 5.02 (1, d, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −6.8 Hz), 5.27 (1, d, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −6.8 Hz), 7.35 (15, m, aryl H); ^{13}C NMR ($CDCl_3$) δ 43.01 (C-2), 75.31 (C-6), 79.87 (C-4), 89.19 (C-5); calcd for M^+, m/e 316.3988; found, m/e 316.3986.

4,4,6,6-Tetraphenyl-1,3-dioxane (9). The same procedure as for **8** was used. A first purification was performed by column chromatography on alumina with benzene, followed by recrystallization from isooctane. Further purification was obtained by HPLC on silica with $CHCl_3/CH_3CN$ (98.7/1.3), followed by recrystallization from petroleum ether, which afforded white crystals: mp 214–215 °C; yield 35%; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.45 (2, s, 5-CH_2), 5.39 (2, s, OCH_2O), 7.35 (20, m, aryl H); ^{13}C NMR ($CDCl_3$) δ 43.95 (C-2), 78.77 (C-4 and C-6), 85.91 (C-5); calcd for M^+, m/e 392.4964; found, m/e 392.4961. Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.71; H, 6.12. Found: C, 85.80; H, 6.20.

(20) Ethyl 3-hydroxy-3-phenylpropionate was prepared as described earlier by C. R. Hauser et al.[21] Yield 58%; bp 155–157 °C (12 mmHg).

(21) C. R. Hauser and D. S. Breslow, "Organic Syntheses," Wiley, New York, 1955, Vol. 3, p 408.

(22) Ethyl 3-hydroxy-3,3-diphenylpropionate was prepared as described earlier by C. R. Hauser et al.[23] Yield 24%; mp 86–87 °C.

(23) C. R. Hauser and W. R. Dunnavant, *J. Org. Chem.* **25**, 1296 (1960).

(24) G. Swaelens, Ph.D. Thesis, R.U.G., 1971.

4,4-Diphenyl-1,3-dioxane (13). The same procedure as for 8 was used. Purification was obtained by HPLC on silica with CH_2Cl_2/CH_3CN (98.8/1.2), followed by recrystallization from petroleum ether, which afforded white needles: mp 91–92 °C; yield 42%; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.50 (2, t, 5-CH_2, $J_{H_5H_4}$ = 5.40 Hz), 3.96 (2, t, 4-CH_2, $J_{H_5H_4}$ = 5.40 Hz), 4.96 (2, s, OCH_2O), 7.35 (10, m, aryl H); ^{13}C NMR ($CDCl_3$) δ 35.52 (C-2), 63.79 (C-6), 79.37 (C-4), 89.20 (C-5); calcd for M^+, m/e 240.3012; found, m/e 240.3017.

1,1,3,3-Tetraphenyl-3-methoxypropanol (5). Monomethyl ether **5** was obtained by a Williamson ether synthesis in which the monosodium alkoxide of diol **4** was allowed to react with CH_3I in DMF during 10 h at room temperature. After purification by column chromatography on alumina with hexane/CH_2Cl_2 (80/20), followed by recrystallization from MeOH, white crystals were obtained: mp 100–101 °C; yield 82%; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.17 (3, s, OCH_3), 3.65 (2, s, 2-CH_2), 6.00 (1, s, OH), 7.35 (20, m, aryl H). Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.28; H, 6.60. Found: C, 85.56; H, 6.55.

1,1,3,3-Tetraphenyl-1,3-dimethoxypropane (15). Dimethyl ether **15** was obtained by a Williamson ether synthesis, in which the disodium alkoxide of diol **4** was allowed to react with CH_3I in THF during 8 h at room temperature. Chromatography on alumina with hexane/CH_2Cl_2 (90/10) followed by recrystallization from MeOH/CH_2Cl_2 (70/30) resulted in white crystals: mp 173–174 °C; yield 88%, ^1H NMR ($CDCl_3$, 60 MHz) δ 2.30 (6, s, OCH_3), 3.60 (2, s, 2-CH_2), 7.45 (20, m, aryl H). Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.29; H, 6.86. Found: C, 84.99; H, 6.91.

1,1,3-Triphenyl-1,3-dimethoxypropane (14). The same procedure as for **15** was used. A first purification was performed by column chromatography on alumina with hexane/CH_2Cl_2, (90/10), followed by recrystallization from EtOH/H_2O (95/15). Further purification was obtained by HPLC on silica with CH_2Cl_2/CH_3CN (98.8/1.2), which resulted in white crystals: mp 78–79 °C; yield 75%; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.65 (1, dd, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −14.5 Hz, $J_{H_{2a}H_3}$ = 4 Hz), 2.90 (3, s, 3-OCH_3), 2.95 (3, s, 1-OCH_3), 3.00 (1, dd, 2-CH_aH_b, $J_{H_{2b}H_{2a}}$ = −14.5 Hz, $J_{H_{2b}H_3}$ = 6 Hz), 4.95 (1, dd, 3-CH, $J_{H_3H_{2a}}$ = 4 Hz, $J_{H_3H_{2b}}$ = 6 Hz), 7.30 (15, m, aryl H). Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.13; H, 7.23. Found: C, 83.27; H, 7.31.

1-Methoxy-1-phenylethane (12). The same procedure as for **5** was used. Purification by preparative GLC (2 m, $^3/_8$ in. glass column, 10% Carbowax 20 M, 160 °C isothermal), followed by kugelröhr distillation at 0.1 mmHg, yielded a colorless oil yield 85%; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.47 (3, d, 2-CH_3, $J_{H_3H_1}$ = 6.7 Hz), 3.30 (3, s, OCH_3), 4.40 (1, q, 1-CH, $J_{H_1H_3}$ = 6.7 Hz), 7.50 (5, m, aryl H). Anal. Calcd for $C_9H_{12}O$: C, 79.41; H, 8.82. Found: C, 79.80; H, 8.79.

Acknowledgment. We are indebted to the N.F.W.O., the F.K.F.O., the University of Leuven Research Fund, the University Centre of Limburg, and the Ministry of Scientific Programming for financial support. Dr. Antheunis is acknowledged for supplying us with a sample of diol **11** and for the use of his NMR equipment.

Registry No. *meso*-**1**, 5381-86-2; (±)-**2**, 5355-61-3; **3**, 14593-41-0; **4**, 4705-01-5; **5**, 87156-58-9; *cis*-**6**, 30630-83-2; *trans*-**7**, 87156-59-0; **8**, 30693-18-6; **9**, 87156-60-3; **10**, 13961-05-2; **11**, 93-56-1; **12**, 4013-34-7; **13**, 5702-27-2; **14**, 87156-61-4; **15**, 87156-62-5.

Nitrogen Effects in Photoreactions. Photochemistry of Iminoquinones with Olefins

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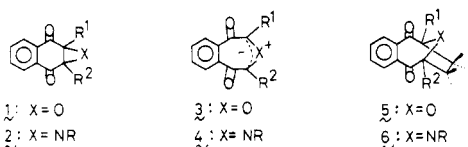
Received March 7, 1983

The photochemistry of epoxyquinones **1** and iminoquinones **2**, which are electronic analogues, was investigated. Upon irradiation with olefins, they afforded cycloadducts **5** and **6**, respectively. The order of relative reactivity (k_r/k_d) of the intermediate (**3** or **4**) with olefin was consistent with frontier orbital theory. The limiting quantum yields (ϕ_{max}) of **2** (~0.01) were about 50 times smaller than those of **1** (~0.5). Absorption and emission spectra revealed that **1** had a typical $n\pi^*$ lowest excited state and **2** had a rather large CT character. This difference of excited state character may be responsible for the differences in photochemical reactivity. Cycloadducts **5** from epoxyquinones **1** underwent further photorearrangement ($\phi \sim 0.1$), whereas cycloadducts **6** were inert ($\phi < 10^{-4}$) photochemically. Examination of the reason for the inertness of **6** revealed that the spatial location of the π system of the arylamino chromophore and that of the phthaloyl chromophore was very critical for the interaction between these two intramolecular chromophores and consequently for the photostability of adducts.

The photochemistry of 2,3-epoxy-2,3-dihydro-1,4-naphthoquinones (**1**), which are easily prepared by oxidation of the corresponding 1,4-naphthoquinones, has been studied extensively, and their photochemical behavior has been elucidated rather well.[1] Nonsubstituted or 2-alkyl substituted epoxyquinones undergo photoreactions characteristic of the carbonyl chromophore. They abstract hydrogen from hydrogen donors[1a] or form oxetanes with olefins.[1b] 2-Aryl or 2,3-disubstituted epoxyquinones, however, react as carbonyl ylides (**3**) or 1,3-diradicals via C–C bond cleavage of the oxirane ring. When olefins,[1b] carbonyl compounds,[1c] singlet oxygen,[1d] or alcohols were present, these epoxyquinones reacted with them to afford adducts that underwent further photorearrangements. The photochemistry of 2,3-imino-2,3-dihydro-1,4-naphthoquinones (**2**), which are electronically analogous to epoxyquinones **1**, is also of interest but is quite unknown. As the result of our syntheses of compounds of type **2**[2] we now report their photochemical reactions with olefins.



A. Padwa and his co-workers have studied the photochemistry of aziridinyl ketones and observed (a) photo-

(1) (a) Maruyama, K.; Arakawa, S. *J. Org. Chem.* **1977**, *42*, 3793. (b) Arakawa, S. *Ibid.* **1977**, *42*, 3800. (c) Maruyama, K.; Osuka, A. *Chem. Lett.* **1979**, 77. (d) Maruyama, K.; Osuka, A.; Suzuki, H. *J. Chem. Soc., Chem. Commun.* **1980**, 723. (e) Osuka, A.; Suzuki, H. *Chem. Lett.* **1981**, 201. (f) Maruyama, K.; Osuka, A.; Suzuki, H. *Ibid.* **1980**, 919.

(2) Maruyama, K.; Ogawa, T. *Chem. Lett.* **1981**, 1027.

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