169.1, 172.3, 174.8; FAB mass spectrum (Ar, positive mode), m/z 472 (M^+, 100), 458 (5).

Deprotection by Hydrogen Fluoride. (i) Low HF Treatment. H-Tyr(PO_3Me_2)-OH·HCl (14) (0.10 g, 0.25 mmol) was treated with HF/Me_2S/m-cresol (2.5:6.5:1.0 v/v, 10 mL) at 0 °C for 2 h. HF was removed under reduced pressure, the residue was washed with diethyl ether (5 × 50 mL) and then dissolved in water (50 mL). Lyophilization gave a yellow solid (127 mg). Quantitative amino acid analysis of the crude product by RP HPLC (C8) (0–30% solvent B in 30 min) showed it to be a mixture of H-Tyr-OH (15) (4.9 min) and H-Tyr(PO_3Me_2)-OH (20.9 min) in a 9:1 ratio (established by comparison with authentic samples).

(ii) High HF Treatment. H-Tyr(PO_3Me_2)-OH·HCl (0.10 g, 0.25 mmol) was treated with 5% anisole/HF (5 mL) at 0 °C for 45 min. The liquid HF was removed under reduced pressure, and the residue was dissolved in water (50 mL), washed with diethyl ether (5 × 50 mL), and lyophilized from water to give a white solid (80 mg). Amino acid analysis (as for i) indicated H-Tyr-OH and H-Tyr(PO_3Me_2)-OH in a 15:85 ratio.

(iii) High HF Treatment of H-Tyr(PO_3H_2)-OH. L-Phosphotyrosine (50 mg, 0.20 mmol) was treated with 5% anisole/HF (5 mL) for 45 min at 0 °C. The liquid hydrogen fluoride was removed under reduced pressure and the residue was isolated (as for method i). Quantitative amino acid analysis as in method i showed the residue to be H-Tyr-OH.

Tyrosylleucylglycine Hydrogen Fluoride (14, H-Tyr-Leu-Gly·HF). Tripeptide, H-Tyr(PO_3H_2)-Leu-Gly-OH·TFA[7] (0.10 g, 0.18 mmol), was treated with liquid HF/10% anisole (10 mL) for 45 min at 0 °C. The liquid HF was then evaporated under reduced pressure, and the residue was triturated successively with diethyl ether (3 × 30 mL) and ethyl acetate/diethyl ether (3:1) (3 × 30 mL) and dried under high vacuum to give tripeptide **17** (0.07 g, 85%) as a white solid: ^{13}C NMR (D_2O) δ 20.9, 21.8, 24.0 35.9, 39.9, 41.1, 52.2, 54.2, 115.8, 125.2, 130.8, 155.1, 168.7, 172.9, 173.7.

Dimethyl *N,N*-Diethylphosphoramidite (15). A solution of methanol (3.20 g, 100.0 mmol) and triethylamine (12.12 g, 120.0 mmol) in dry diethyl ether (40 mL) was slowly added to a solution of dichloro *N,N*-diethylphosphoramidite (8.65 g, 50.0 mmol) in dry diethyl ether (20 mL) at −20 °C such that the temperature of the solution was maintained below −10 °C. On completion of addition, the solution was vigorously stirred at 20 °C for 2 h, and then 10% Na_2CO_3 (20 mL) was added. The solution was transferred to a separating funnel using diethyl ether (40 mL), and the aqueous phase was discarded. The organic phase was washed with 10% Na_2CO_3 (30 mL) and NaCl (saturated, 30 mL) and dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. Distillation of the crude liquid residue gave **15** as a pungent, clear liquid (5.2 g, 63%): bp 38–40 °C (2.0 mmHg); ^1H NMR ($CDCl_3$) δ 1.06 (d, J_{HH} = 7.08 Hz, 6 H, NCH_2CH_3), 3.07 (dq, J_{HH} = 7.08 Hz, J_{PH} = 9.08 Hz, 4 H, NCH_2CH_3), 3.39 (d, J_{PH} = 12.7 Hz, 6 H, $POCH_3$); ^{13}C NMR ($CDCl_3$) δ 14.1 (d, J_{PC} = 2.9 Hz, NCH_2CH_3), 36.3 (d, J_{PC} = 20.5 Hz, NCH_2CH_3), 48.9 (d, J_{PC} = 14.7 Hz, $POCH_3$); ^{31}P NMR ($CDCl_3$) δ +150.2.

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Registry No. 1, 119255-37-7; 2, 127103-00-8; 3, 92264-99-8; 4, 127103-01-9; 5, 127103-02-0; 6, 118903-64-3; 7, 15761-39-4; 8, 118903-66-5; 9, 118903-67-6; 10, 118903-68-7; 11, 118903-70-1; 12, 127103-03-1; 13, 127129-84-4; 14, 118892-05-0; TFMSA, 1493-13-6; TFA, 76-05-1; TMSBr, 2857-97-8; TMSOTf, 27607-77-8; BrMaq, 7598-10-9; $(MeO)_2PNEt_2$, 20621-25-4; BOC-Tyr-OH, 3978-80-1; $ClP(O)(OMe)_2$, 813-77-4; BOC-Val-OH, 13734-41-3; Me_2S, 75-18-3; 3-MeC_6H_4OH, 108-39-4; PhSMe, 100-68-5; HF, 7664-39-3; H-Tyr(PO_3Me_2)-OH·HCl, 118903-62-1; H-Tyr-OH, 60-18-4; H-Tyr(PO_3H_2)-OH, 21820-51-9; H-Tyr(PO_3H_2)-Leu-Gly-OH·TFA, 118892-04-9; Cl_2PNEt_2, 1069-08-5.

Regioselective Acylation of 6-Deoxy-L- and -D-hexosides through Lipase-Catalyzed Transesterification. Enhanced Reactivity of the 4-OH Function in the L Series

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Porcine pancreatic, *Candida cylindracea*, and *Pseudomonas fluorescens* lipases, suspended in organic solvents, were used to regioselectively acylate methyl α-L- and α-D-rhamnopyranoside and methyl α-L- and α-D-fucopyranoside. While the D-sugars always gave the 2-butyrate as the main product, their L enantiomers showed a different regioselectivity; however, by proper selection of the enzyme, in the L series the rather unreactive 4-OH function could be preferentially acylated.

Introduction

Alcoholic functions of sugars markedly differ in their reactivity.[1] Primary hydroxyl group is obviously the most reactive, but among the secondary groups a wide range of reactivities can be observed. Orientation (equatorial or axial) or position of the hydroxyl groups are the two variables which mainly modulate this reactivity; the 4-OH has often a very low reactivity toward several reagents. In fact, selective monoacylation of glucose, galactose, etc. in this position can be hardly obtained.[1,2]

Hydrolytic enzymes were recently used as catalysts for regioselective esterification of sugars when suspended in organic solvents in conditions allowing a transesterification between an activated ester and the polyhydroxylated moiety.[3-5] D-Glucose, D-mannose, and D-galactose have

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(1) Haines, A. H. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 11–109.
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Table I. Enzymatic Butyrylation of Compounds 1a–4a

entry	substrate	enzyme	T, °C	time, days	overall yield, %	% monoesters b (C-2)	c (C-3)	d (C-4)
1	1a	PPL[a]	45	12	80	8	4	88
2	2a	PPL[b]	45	12	66	4	28	68
3	3a	PPL[a]	45	12	8	41	27	32
4	4a	PPL[b]	45	4	83	94	d	6
5	1a	CCL[c]	45	3	89	d	35	65
6	2a	CCL[c]	45	7	66	4	89	7
7	3a	CCL[c]	45	7	65	63	34	3
8	4a	CCL[c]	45	3	90	78	15	7
9	1a	PFL[a]	25	12	63	1	3	96
10	2a	PFL[b]	25	12	45	2	1	97
11	3a	PFL[a]	25	12	42	96	1	3
12	4a	PFL[b]	25	4	88	96	d	4

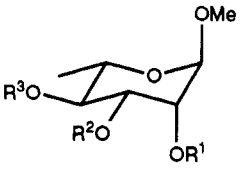
[a] Solvent: tetrahydrofuran. [b] Solvent: tetrahydrofuran–pyridine, 4:1. [c] Solvent: methylene chloride–acetone, 4:1. [d] Traces (by NMR).

been submitted to this reaction;[3] the lipase–trichloroethyl butyrate system first furnished the monoester on the primary 6-position;[6] then, further reaction transformed the so obtained 6-butyrates into the 2,6- and/or 3,6-diester derivatives, depending on the substrate and on the enzyme used. The 4-position, chemically the least reactive, was found unreactive toward the enzymatic reagent system.

We asked whether this low reactivity could be ascribed to the presence of a polar (acyloxy)methyl group on the C-6 position and chose[7] the two naturally occurring 6-deoxy sugars L-rhamnose and L-fucose with the aim to verify whether some enzymatic acylating system is able to esterify their unreactive 4-OH. The results obtained[4] utilizing the porcine pancreatic lipase–trifluoroethyl butyrate system were found complementary to those obtained with chemical butyrylating agents and different from the results concerning the secondary hydroxy functions of D-glucose, D-mannose, and D-galactose. So, we decided to extend our investigation to the D series by studying D-rhamnose and D-fucose in order to ascertain the influence of the absolute configuration on the regioselectivity of the acylation. Moreover, two other cheap and easily available hydrolytic enzymes, *Candida cylindracea* and *Pseudomonas fluorescens* lipase, have been also tested as catalysts for these transesterification reactions.

Results and Discussion

We have used the methyl α-pyranoside derivatives (**1a–4a**) of the four sugars under investigation for two reasons; they are more soluble in organic solvents than the parent 6-deoxyhexoses (in solvents of low polarity lipases usually work better than in solvents of high polarity);[8] analysis and separation of the products in the reaction mixture are easier in the presence of only one anomer instead of the two present for the sugars in the hemiacetalic form. Moreover, methyl glycopyranosides are commonly used as starting material in the synthesis of biologically important oligosaccharides.



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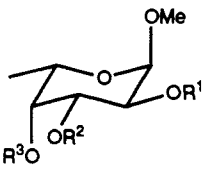

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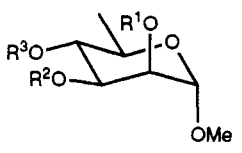

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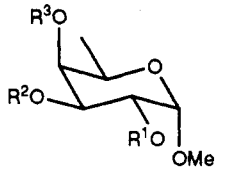

4

a: $R^1=R^2=R^3=H$; **b**: $R^1=COPr$, $R^2=R^3=H$;
c: $R^1=R^3=H$, $R^2=COPr$; **d**: $R^1=R^2=H$, $R^3=COPr$.

Three commercially available crude enzyme preparations, porcine pancreatic lipase (PPL), *Candida cylindracea* lipase (CCL), and *Pseudomonas fluorescens* lipase (Lipase P Amano, PFL) were used throughout our study. As a compromise between solubility of substrates and good activity of enzymes, tetrahydrofuran was the solvent of choice for PPL and PFL (pure in the case of **1a** and **3a**, in a 4:1 mixture with pyridine in the case of **2a** and **4a**) and methylene chloride–acetone, 4:1, for CCL. Preliminary tests with the usually utilized[3-5] acyl carriers, 2,2,2-trichloroethyl butyrate (TCEB), 2,2,2-trifluoroethyl butyrate (TFEB), and the enol esters vinyl acetate and isopropenyl acetate, were carried out. The two latter compounds gave very slow reactions with low selectivity. On the contrary, both trihaloethyl esters worked well, but the conversion in the case of TFEB was found about 50% faster than in the case of TCEB, though they showed the same regioselectivity. For these reasons TFEB was used throughout the work.

All the four substrates **1a–4a** were then submitted to the three enzymatic systems. The corresponding monobutyrates **1b–d**, **2b–d**, **3b–d**, **4b–d** were obtained in mixtures whose compositions are summarized in Table I. The reactions were carried out until the starting material almost completely disappeared; otherwise they were stopped after 12 days in the case of PPL and PFL and 7 days in the case of CCL. The composition of the monoesters fractions,

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(7) Preliminary results have been published in ref 4.

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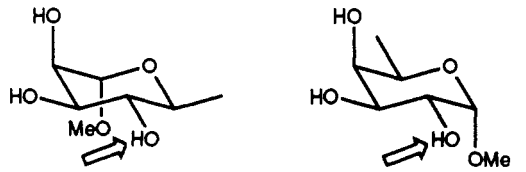

Figure 1.

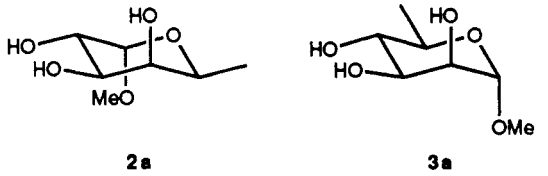

Figure 2.

obtained by column chromatography from the crude reaction mixture, was determined by ^{1}H NMR.[4]

In the case of PPL (entries 1–4) the extent of the conversion was very different for the four cases, ranging from an isolated monoesters yield of 83% after 4 days in the case of the D-fucoside **4a** (entry 4) to 8% after 12 days in the case of the D-rhamnoside **3a** (entry 3). D-Fucoside **4a**, the best substrate, was mainly butyrylated at 2-OH. Conversely, L-rhamnopyranoside **1a** and L-fucopyranoside **2a** were butyrylated by the same enzyme at 4-OH (entries 1 and 2), though **2a** was converted less efficiently and with less regioselectivity than **1a**. D-Rhamnopyranoside **3a** was recovered practically unreacted as only 8% conversion was obtained after 12 days with a totally random distribution of the products (entry 3).

The results obtained with CCL (entries 5–8) were only in some respects similar to that obtained with PPL. As in that case, compounds **1a** and **4a** were the best substrates, as they were very efficiently converted (entries 5 and 8); the regiochemistry of the reaction was the same as with PPL, but a low selectivity was observed. On the contrary, compounds **2a** and **3a** gave with CCL results different from those obtained with PPL. They were both good substrates, but **2a** was esterified on 3-OH and **3a** on 2-OH (entries 6 and 7).

PFL showed in all the four cases a very good regioselectivity, always furnishing in the L series the 4-butyrate and in the D series the 2-butyrate with only minor traces of the other monobutyrates (entries 9–12). Once again **4a** was the best substrate (entry 12), while **1a**, **2a**, and **3a** needed longer reaction times to give more (**1a**) or less (**2a** or **3a**) satisfactory yields.

Our results show that two sugars, D-fucoside **4a** and L-rhamnoside **1a**, are the best substrates for all the enzymes, though they belong to different series and are acylated at different positions. These findings could be rationalized hypothesizing that the orientation of the sugars at the active site of the enzymes is mainly determined by the three free hydroxy groups. In fact, Figure 1 clearly shows that **1a** and **4a** possess the same arrangement of these alcoholic functions, i.e. axial–equatorial–equatorial (AEE), and that the reaction always occurs at the same terminus of this alcoholic triplet. Substitution at C-1 and C-5 seems to play only a minor role.

The other two sugars L-fucoside **2a** and D-rhamnoside **3a** have an equatorial–equatorial–axial (EEA) sequence of the hydroxyl groups (Figure 2). They are less easily converted as, probably, they have to find their best interaction with butyryl enzymes in other orientations than **1a** and **4a**. A rationalization is not easy; in most of the cases the substrates are acylated at the same axial terminus of the EEA triplet (entries 2, 7, 10, 11), but in a case the central hydroxyl groups is acylated (entry 6) and in a case both conversion and regioselectivity are extremely poor (entry 3).

So, in the D series the 2-*O*-butyryl derivatives are always the main products of the enzymatic transesterifications of 6-deoxyhexoses; in the L series more interesting results are obtained from a preparative point of view; in fact, the regioselective butyrylation at the 4-position can be obtained in good yields. The C-4 alcoholic group of 6-deoxy sugars has very little reactivity toward chemical acylating agents,[9] and it is noteworthy that enzymatic acylating systems can overcome this problem.

In conclusion, our results indicate that enzymatic butyrylation becomes complementary to chemical acylation as it can afford products not easily obtainable by direct chemical transformations. The large enhancement of the reactivity of the 4-OH function, with respect to the other secondary hydroxyl groups, seems confined to sugars belonging to the L series which widely occur, however, throughout nature; 4-butyrates, so obtained, may result in useful intermediates for the synthesis of more complex structures.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded with a Bruker AM-500 or with a Bruker AC-200 spectrometer in deuteriochloroform solutions. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. Analytical TLC was carried out on Merck 60 F_{254} silica gel plates (0.25 mm thickness), and the spots were detected by spraying with 50% aqueous H_2SO_4 and heating at 110 °C. Column chromatography was performed with Merck 60 silica gel (70–230 mesh). Porcine pancreatic lipase (Type II) (PPL) and *Candida cylindracea* lipase (Type VII) (CCL) were obtained from Sigma; *Pseudomonas fluorescens* lipase (Lipase P) (PFL) was a generous gift from Amano Pharmaceutical Co., Frankfurt. CCL was used as received; PPL and PFL were kept under vacuum prior to use in order to lower the water content to 0.5%. Tetrahydrofuran and pyridine were distilled just prior to use from, respectively, sodium/benzophenone and calcium hydride. Methylene chloride and acetone were dried over 3-Å molecular sieves.

General Procedure for PPL-Catalyzed Transesterification of Compounds 1a–4a. The sugar substrate (200 mg) was dissolved into the solvent (4 mL), tetrahydrofuran for **1a**, **3a**, tetrahydrofuran–pyridine, 4:1, for **2a**, **4a**; TFEB (1 mL) and PPL (1 g) were added, the suspension was stirred at 45 °C, and the reaction mixture was monitored by TLC for the conversion. At the end of the reaction, the enzyme was filtered off and the solvent was removed by evaporation under reduced pressure. The monobutyrates fraction was separated by column chromatography (eluant toluene–acetone, 3:1) and analyzed by ^{1}H NMR for the determination of the product ratios.

Pure monoesters from **1a** (or **3a**) could be obtained by column chromatography eluted with toluene–acetone, 3:1; first the monobutyrate **1c** (or **3c**) eluted, then a mixture of **1b** (or **3b**) and **1d** (or **3d**). The last two products could be separated by careful column chromatography eluted with chloroform–methanol, 20:1. Pure monoesters from **2a** (or **4a**) could be obtained similarly: the first column gave a mixture of **2b** (or **4b**) and **2c** (or **4c**) and pure **2d** (or **4d**); the second column gave pure **2b** (or **4b**) and **2c** (or **4c**) from their mixture.

For the physical data of the monobutyrates **1b–d** and **2b–d**, see ref 4. **3b**: oil; $[\alpha]_D^{20}$ +29° (*c* 1.0, $CHCl_3$). **3c**: oil; $[\alpha]_D^{20}$ +31° (*c* 1.1, $CHCl_3$). **3d**: mp 63.5–65 °C; $[\alpha]_D^{20}$ +94° (*c* 1.2, $CHCl_3$). **4b**: oil; $[\alpha]_D^{20}$ +144° (*c* 1.1, $CHCl_3$). **4c**: oil; $[\alpha]_D^{20}$ +177° (*c* 1.5,

(9) Chemical butyrylation of **1a** with 1 equiv of butyryl chloride furnishes[4] a monoester fraction **1b**:**1c**:**1d** whose percentage composition is 19:77:4. In the same conditions for **2a** a mixture of **2b**:**2c**:**2d** is obtained[4] in a ratio 69:31:traces.

$CHCl_3$). **4d**: oil; $[\alpha]_D^{20}$ +135° (*c* 1.2, $CHCl_3$). ^1H NMR chemical shifts of **3b–d** and **4b–d** were nearly identical with those described for **1b–d** and **2b–d** in ref 4.

General Procedure for CCL-Catalyzed Transesterification of Compounds 1a–4a. All conditions but the solvent (methylene chloride–acetone, 4:1) were the same as in the above procedure with PPL.

General Procedure for PFL-Catalyzed Transesterification of Compounds 1a–4a. All conditions but temperature (25 °C) were the same as in the above procedure with PPL.

Regioselective Synthesis of Substituted Rubrenes

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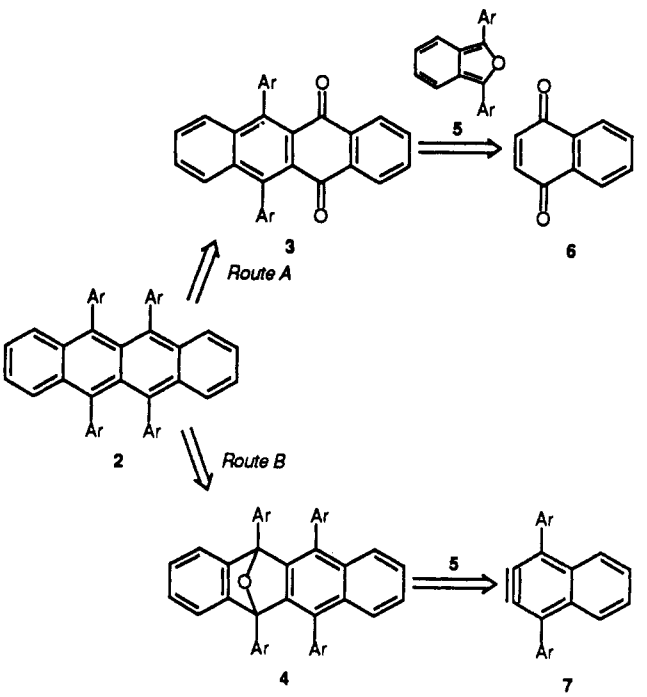
The development of two complementary synthetic routes to 5,6,11,12-tetraphenylnaphthacene (rubrene) derivatives is described. In one approach, selective nucleophilic addition of aryllithiums to diarylnaphthacenequinones (**13**, **14**, **16**), followed by HI aromatization of the corresponding diols, allows for the convenient preparation of a wide variety of selectively functionalized rubrenes. Symmetrically and unsymmetrically di- and tetrasubstituted rubrenes have been prepared, as well as several "end-capped" versions. In a second route, cycloaddition of 1,3-diphenylisobenzofuran with the naphthyne **7** (Ar = Ph) followed by Lewis acid mediated deoxygenation of the resultant oxo-bridged adduct gives rubrene in a particularly convergent manner. Elaboration through the use of substituted isobenzofurans (i.e. **9–11**) allows for the analogous preparation of substituted rubrenes (**45–47**).

Introduction

The polycyclic aromatic hydrocarbon rubrene (**1**; 5,6,11,12-tetraphenylnaphthacene) has been studied extensively for its wide varity of interesting properties, including electrochemiluminescence,[1a] enhanced chemiluminescence,[1b] fluorescence,[1c] photoconductivity,[1d] photooxidation,[1e] and others.[2] Rubrene and related polyaromatics have also proven to be particularly valuable tools for the trapping of singlet oxygen in a variety of chemical processes.[3] This well-studied hydrocarbon appeared to have considerable potential as the basis of a new host for small organic molecules if the shallow hydrophobic cleft formed by the intersecting aryl rings could be appropriately functionalized with complementary binding groups. Structural investigations[4] show that the phenyl rings of **1** are approximately perpendicular to the planar naphthacene core and thus provide a number of potential sites

Scheme I



(1) For recent representative examples, see the following. (a) Electrochemiluminescence: Engstrom, R. C.; Johnson, K. W.; DesJarlais, S. *Anal. Chem.* **1987**, *59*, 670. Itoh, K.; Honda, K.; Sukigara, M. *J. Electroanal. Chem.* **1980**, *110*, 277. Dunnet, J. S.; Voivnov, M. *J. Electroanal. Chem.* **1978**, *89*, 181. Dunnet, J. S.; Voivnov, M. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 853. Yeh, L.-S. R.; Bard, A. J. *Chem. Phys. Lett.* **1976**, *44*, 339. Keszthelyi, C. P.; Tokel-Takvoryan, N. E.; Bard, A. J. *Anal. Chem.* **1975**, *47*, 249. Maloy, J. T.; Bard, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 5968. Pighin, A. *Can. J. Chem.* **1973**, *51*, 3467. Maricle, D. L.; Maurer, A. *J. Am. Chem. Soc.* **1967**, *89*, 188. (b) Enhanced chemiluminescence: Larena, A.; Martinez-Urreaga, J. *Spectrosc. Lett.* **1985**, *18*, 463. Adam, W.; Cueto, O.; Yany, F. *J. Am. Chem. Soc.* **1978**, *100*, 2587. Adam, W.; Cancio, E. M.; Rodriguez, O. *Photochem. Photobiol.* **1978**, *27*, 617. (c) Fluorescence: Yee, W. A.; Kuzmin, V. A.; Kliger, D. S.; Hammond, G. S.; Twarowski, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 5104. Liu, D. K. K.; Faulkner, L. R. *J. Am. Chem. Soc.* **1977**, *99*, 4594. Wilson, T. *J. Am. Chem. Soc.* **1969**, *91*, 2387. (d) Photoconductivity: Frankevich, E. L.; Tribel, M. M.; Sokolik, I. A. *Phys. Status Solidi B* **1976**, *77*, 265. Romanets, R. G.; Prock, A.; Zahradnik, R. *J. Chem. Phys.* **1970**, *53*, 4093; (e) Photooxidation: Yamada, M.; Isao, I.; Kurado, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1057. Gsponer, H. E.; Previtali, C. M.; Garcia, N. A. *J. Photochem.* **1987**, *36*, 247. Caminade, A. M.; Khatib, F. E.; Koenig, M.; Aubry, J. M. *Can. J. Chem.* **1985**, *63*, 3203. Aubry, J. M.; Rigaudy, J.; Cuong, N. K. *Photochem. Photobiol.* **1981**, *33*, 149 and 155. Herkstroeter, W. G.; Merkel, P. B. J. *Photochemistry* **1981**, *16*, 331. Turro, N. J.; Chow, M.-F.; Kanfer, S.; Jacobs, M. *Tetrahedron Lett.* **1981**, 3. Harada, Y.; Takahashi, T.; Fujisawa, S.; Kajiwara, T. *Chem. Phys. Lett.* **1979**, *62*, 283.

(2) A CAS Online literature search of rubrene revealed 206 references (1967 to date) dealing with the aforementioned subjects (footnotes 1–5) as well as other miscellaneous topics.

(3) (a) Moureu, C.; Dufraisse, C.; Dean, P. M. *C. R. Acad. Sci.* **1926**, *182*, 1440. (b) *Ibid.* **1926**, *182*, 1584. (c) Wasserman, H. H.; Scheffer, J. R.; Cooper, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 4991.

(4) For a crystal structure of rubrene, see: Akopyan, Z. A.; Avoyan, R. L.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1962**, *3*, 602. Other references dealing with structural or conformational aspects of rubrene include: (a) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981. (b) Bulgarovskaya, I. V.; Vozzhennikov, V. M.; Aleksandrov, S. B.; Bel'skii, V. K. In *Elektron. Org. Mater.*; Ovchinnikov, A. A., Ed.; Nauka: Moscow, 1985; pp 211–3. (c) Takahashi, T.; Harada, Y.; Sato, N.; Seki, K.; Inokuchi, H.; Fujisawa, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 380. (d) Storek, W.; Sauer, J.; Stoesser, R. *Z. Naturforsch., A* **1979**, *34A*, 1334. (e) Henn, D. E.; Williams, W. G.; Gibbons, D. J. *J. Appl. Crystallogr.* **1971**, *4*, 256. (f) Tinland, B. *J. Mol. Struct.* **1969**, *4*, 330. (g) Nakashimi, T. T.; Offen, H. W. *J. Chem. Phys.* **1968**, *48*, 4817. Rotational barriers of related tetra- and diphenylnaphthalene systems have also been investigated. See: (a) Clough, R. L.; Roberts, J. D. *J. Org. Chem.* **1978**, *43*, 1328. (b) Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 3603.