THF (100 mL) at $-105\,^{\circ}$C. The reaction mixture was slowly warmed to $-80\,^{\circ}$C and stirred for 4 h. The resulting purple solid was separated by filtration at $-80\,^{\circ}$C to afford **2a** (1.44 g, 70%). **3a**: A solution of *t*BuLi (4.7 mmol, 2.8 mL of a 1.7 M solution in hexane) was added dropwise to a solution of **1** (2.4 g, 9.4 mmol) in THF (100 mL) at $-105\,^{\circ}$C. The reaction mixture was slowly warmed to room temperature under stirring, and the solvents were removed in vacuo. The residue was washed with *n*-pentane (50 mL), and precipitated LiCl was separated by filtration. Removal of the solvent in vacuo afforded **3a** as beige crystals (1.93 g, 93%; m.p. 148–149 °C).

[7] **3a**: ^{31}P NMR (121 MHz, THF, 303 K): $\delta = 18.9$; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.5$ (m, 36H; CH_2, CH_3); ^{13}C NMR (75.47 MHz, C_6D_6, 303 K): $\delta = 129.3$ (pseudo t, $\Sigma J = 13.4$ Hz; *C*=*C*), 58.9 (s; *C*NP), 42.1 (s; *C*CN), 31.6 (pseudo t, $\Sigma J = 6.3$ Hz; C_2CNP), 17.7 (s, *C*CCN); UV/Vis (1% $BaSO_4$ solution): $\lambda_{max} = 567$ nm; MS (40 eV, EI): *m/z*(%): 436 (22) [M^+], 421 (20) [$M^+ - CH_3$], 401 (4) [$M^+ - Cl$], 296 (13) [$M^+ - C_9H_{18}N$], 230 (20) [$C_{11}H_{18}ClNP^+$], 126 (37) [$C_9H_{18}N^+ - CH_2$], 69 (100) [$C_4H_7N^+$]; correct elemental analysis.

[8] Crystal data for **3a**: $C_{20}H_{36}Cl_2N_2P_2$, $M_r = 437.4$, orthorhombic, space group $P2_12_12_1$ (no. 19), colorless crystals, dimensions $0.50 \times 0.18 \times 0.13$ mm^3, $a = 11.078(1)$, $b = 14.570(2)$, $c = 14.596(1)$ Å, $V = 2355.9(4)$ Å^3, $\rho_{calcd} = 1.233$ Mg m^{-3}, $Z = 4$, $\mu(Cu_{K\alpha}) = 3.81$ mm^{-1}, $T = 200(2)$ K; of 5327 reflections collected, 3833 were symmetry-independent and used for the structure solution (direct methods)[9a] and refinement (full-matrix least squares on F^2, 236 parameters).[9b] Non-hydrogen atoms were refined anisotropically, and H atoms localized by difference electron density and refined with a riding model ($wR2 = 0.136$, $R1 = 0.051$, for $I > 2\sigma(I)$). An empirical absorption correction on the basis of ψ scans was applied; the absolute structure could not be determined reliably. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100757. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[15] The energy optimation at the MP2 level was performed with the Gaussian set of programs: Gaussian94 (Revision D4), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian Inc., Pittsburgh, PA, **1995**.

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[17] All stationary points on the electronic hypersurface were characterized by vibrational analysis based on the method of numerical differentiation of the first-order gradients. Consequently, energy minima possess overall positive vibrational frequencies, and the two transition states display one imaginary vibration. Energy values were obtained from the MCSCF energies after zero-point vibrational correction.

[18] A stable phosphanylcarbene is known;[19] intermediates of this type are also supposed to appear in the thermal rearrangement of 1,3-diphosphacyclobutane-2,4-diyl **2b** to an isomeric 1,3-diphosphapropene.[4]

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Intense Dyes through Chromophore–Chromophore Interactions: Bi- and Trichromophoric Perylene-3,4:9,10-bis(dicarboximide)s[**]

Heinz Langhals[*] and Wolfgang Jona

Dedicated to Professor Heinrich Nöth
on the occasion of his 70th birthday

The UV/Vis spectra of dyes have commonly been controlled by introducing suitable substituents or by altering the chromophore. An interesting alternative is allowing two or more identical chromophores to interact directly, which might be expected to give pronounced effects in color. Perylene-3,4:9,10-bis(dicarboximide)s **1** were chosen as the basic chromophore because of their unusually high chemical and photochemical persistency and their high fluorescent quantum yields.[1] Moreover, the absorption of **1** in the visible region is caused by only one electronic transition,[2] and there are orbital nodes[3] at the nitrogen atoms in the HOMO and LUMO, which make these atoms ideal positions for linking. The thus "closed chromophore" is only negligibly influenced by substituents. The linking of two chromophores of **1** through a longer spacer did not result in a considerable alteration of the UV/Vis spectra.[4–6] Only an appreciable overlap of the chromophors induced a strong exciton absorption at longer wavelengths.[7, 8]

Here we try to adjust the chromophore–chromophore interaction to just an exciton coupling by reducing the separation between two chromophores to the distance of a single bond. Undesired interaction between the chromophores through conjugation is excluded by their orthogonal orientation and linkage at the nitrogen atoms (orbital nodes).

The starting material for the synthesis of such polychromophores are the peryleneimides **3**, which are readily soluble and have a free amino group at one nitrogen atom. Compounds **3**-

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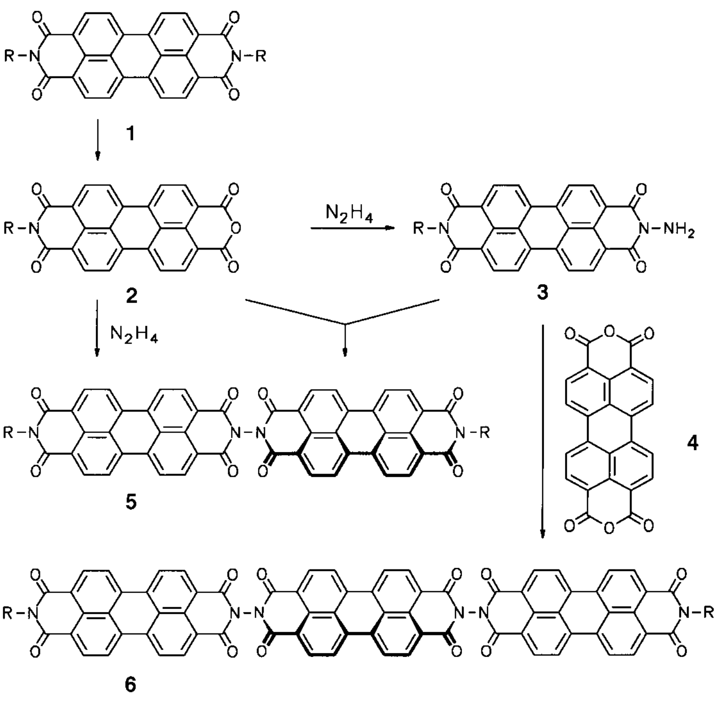

1-3,5,6	R
a	$CH(C_6H_{13})_2$
b	$CH(C_4H_9)_2$
c	$CH(C_7H_{15})_2$
d	$CH(C_8H_{17})_2$
e	$CH(C_9H_{19})_2$
f	2-CH_3-5-*t*-C_4H_9-C_6H_3

Scheme 1. Synthesis of bi- and trichromophoric perylene dyes.

are prepared from perylene anhydride imides **2** and hydrazine or hydrazinium salts under mild reaction conditions (100–130 °C, 0.5–1 h) in molten imidazole (Scheme 1). Aminoimides **3** are condensed with **2** to form bichromophoric perylenes **5**, which can even be directly prepared from **2** and hydrazine if the exact stoichiometry of 2:1 is guaranteed. This requires special care because of the low quantities of hydrazine to be added. An excess of **2** results in a decrease in yield, and an excess of hydrazine provides essentially **3**. Hydrazinium sulfate has been proven to be a source for hydrazine that can be easily dosed.

The expected low solubility of bichromophoric perylenes is a problem for synthesis, purification, and spectroscopic investigation. A notable improvement is brought about by the introducing solubilizing groups such as *sec*-alkyl groups[9] ("swallow-tail substituents") or aryl groups with *tert*-butyl substituents[10] which are linked to the terminal nitrogen atoms of the dyes. The solubility of the dyes so prepared is high enough for all investigations.

Trichromophoric perylene dyes **6** can be prepared in the same manner, in that amino derivative **3** is condensed with perylene-3,4:9,10-tetracarboxylic dianhydride (**4**). This reaction also proceeds under mild conditions in imidazole, and it too requires an exact stoichiometry.

The formamide of **3** (prepared from **3** and anhydrous formic acid, at least 99% at 70 °C) was also used for the condensation, because formamides are more reactive than free amines. This method has no advantages with respect to the yields and purity of **5** or **6**, but is to be favored if the absolute absence of heavy metals in the reaction products is required because no catalyst such as zinc acetate is necessary.

We tried to convert[4] one of the terminal imide groups of **5** into an anhydride group to obtain a building block for dyes with an even larger number of chromophores. However, this concept failed because saponification of the connection of two imides is the easier process. This bond can also be cleaved with hydrazine. Apparently the increase in reactivity of the carbonyl groups through the electron-withdrawing effect of the second imide unit dominates over the sterical shielding.

The bi- and trichromophoric dyes **5** and **6** are lightfast and exhibit structured UV/Vis spectra and a pronounced fluorescence in solution (Figure 1, Table 1). The absorption maxima are more and more bathochomically shifted as the number of chromophores increases. The extinction coefficients of most absorption bands are about two or three times higher than for the monochromophoric dyes. An notable deviation from this rule is observed for the most bathochromic vibration band of the bi- and trichromophoric dyes: An

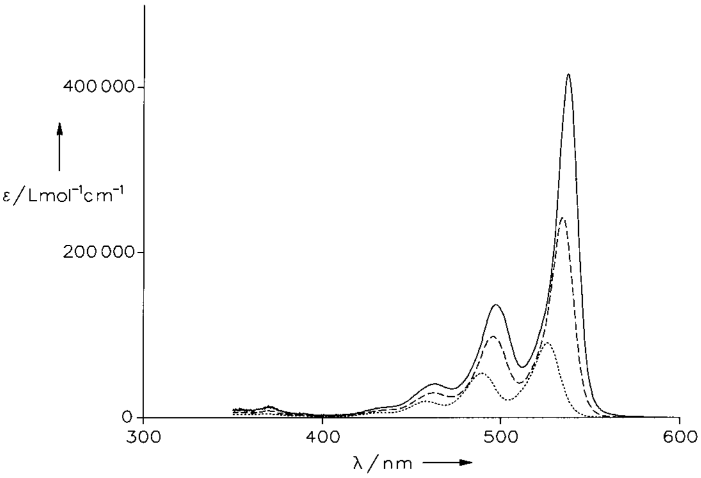

Figure 1. UV/Vis absorption spectra of **1a** (⋯; color coordinates:[14] $x = 0.3622$, $y = 0.3151$, $Y = 78.29$, 2°, normlight C, $T_{min} = 0.1$), **5a** (– – –; color coordinates: $x = 0.3467$, $y = 0.2940$, $Y = 77.46$), and **6a** (—; color coordinates: $x = 0.3409$, $y = 0.2901$, $Y = 78.47$) in $CHCl_3$.

Table 1. Yields, electron spectroscopic data, and R_f values for the perylene dyes **5** and **6**.

Entry	Yield [%][a]	UV/Vis[b] λ_{max} [nm] (ε [L mol^{-1} cm^{-1}])	Fluoresc.[b, c] λ_{max} [nm]	Solid[d] λ_{max} [nm]	R_f[e]
5a	39	535 (241 800), 496 (97 700)	540	530	0.33
5b	41	534 (230 100), 496 (94 700)	539	623	0.11
5c	29	535 (241 700), 496 (97 800)	539	534	0.40
5d	56	535 (242 000), 496 (98 300)	539	–	0.42
5e	31	534 (239 200), 496 (97 000)	538	534	0.21
5f	38	535 (250 200), 495 (100 600)	540	–	0.84[f]
6a	15	538 (416 900), 497 (135 000)	543	–	0.34
6c	8	537 (407 000), 497 (134 000)	544	–	–
6e	57	538 (422 100), 497 (139 500)	544	–	0.37

[a] Yield of isolated, analytically pure substance. [b] In $CHCl_3$. [c] Fluorescence spectrum. [d] Solid-state fluorescence. [e] Silica gel, $CHCl_3$/1-butanol (40/1). [f] $CHCl_3$/ethanol (10/1).

additional sharp band seems to be "sitting on" the normal vibration band, and a higher extinction coefficient is observed. This effect is even more pronounced for the trichromophoric perylene dyes (Figure 1). If one takes extinction coefficients of 85000 to 95000 $L mol^{-1} cm^{-1}$ as being "normal" for **1**, the value for bichromophoric dyes (ε = 240000 $L mol^{-1} cm^{-1}$) is much more than twice that for **1**, and an extinction coefficient of 420000 $L mol^{-1} cm^{-1}$ for the trichromophoric dyes **6** is more than 135000 $L mol^{-1} cm^{-1}$ higher than three times the value for **1**. Such high extinction coefficients have not yet been reached by simple perylene dyes, and the multichromophoric dyes can therefore be considered as "intense dyes". The spectral characteristics of the bi- and trichromophoric dyes can be explained on the basis of an exciton interaction. Although the Davydov splitting becomes vanishingly low because of the relatively weak coupling between the chromophores, the exciton band[11] persists and falls in the same spectral region as the normal absorption of the individual chromophores. It is of interest that the absorption band at longest wavelengths is much sharper than the other absorption bands of the perylene dye. The low half-width value is useful for obtaining very brilliant shades of color, and the new principle may also be of interest for practical applications.

All bi- and trifluorophoric dyes are highly fluorescent; fluorescent quantum yields of 98, 89, 97, and 100% have been measured for **5a**, **6a**, **6c**, and **6e**, respectively.[12] The fluorescence bands are also shifted to increasingly longer wavelengths with an increasing number of linked chromophores and exhibit the vibration structure which is typical for perylene dyes. The bathochromically shifted fluorescence is also of interest for practical applications.

Perylene dyes **1** tend to aggregate at high concentration.[13] This tendency is enhanced from bichromophoric to trichromophoric dyes and is very pronounced for the latter. However, spectra of nonaggregated dyes are obtained for concentrations below 5×10^{-6} $mol L^{-1}$ (see Figure 1). A further bathochromic shift along with a pink coloration is obtained for the aggregates; this is typical for J aggregates. An indicator for J aggregates is their pronounced fluorescence (λ_{max} = 630 nm), which is not observed for H aggregates.[14] Because of their long wavelengths J aggregates are of technical interest. On the other hand, the chain length of the N-terminal substituents can be made sufficiently long for the exclusion of aggregation in homogeneous solution (see also the increasing quantum yields from **6a** to **6e** as a result of a decreasing tendency to aggregate).

The principle of color strengthening through exciton interactions described here can certainly be generalized. It is therefore also of interest for other dyes.[15]

Experimental Section

3a: Compound **2a** (2.0 g, 3.5 mmol), hydrazine hydrate (350 mg, 6.9 mmol), and imidazole (7 g) were heated (130 °C, 60 min) and then treated with ethanol/2 N HCl (50 mL, 1/1). The solid precipitate was washed with methanol/water, dried (100 °C), and purified by column chromatography (neutral Al_2O_3, $CHCl_3$/ethanol (20/1) and then silica gel, $CHCl_3$/ethanol (20/1)) to give **3a** (830 mg, 40%). M.p. 332–334 °C; R_f (silica gel, $CHCl_3$/ethanol (10/1)) = 0.80; R_f (silica gel, $CHCl_3$/ethanol 20/1) = 0.61; IR (KBr): $\tilde{\nu}$ = 2956 (m), 2927 (s), 2857 (m), 1699 (s), 1658 (s), 1595 (s), 1578 (m), 1404 (s), 1350 (s), 1255 (s) 805 (s), 739 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ = 0.81 (t, 6H, 2 CH_3), 1.28 (m_c, 16H, 8 CH_2), 1.88 (m_c, 2H, 2 α-CH_2), 2.24 (m_c, 2H, 2 α-CH_2), 5.16 (m_c, 1H, NCH), 5.48 (s, 2H, NH_2), 8.33 (d, ^3J = 8.2 Hz, 2H, perylene), 8.41 (d, ^3J = 8.2 Hz, 2H, perylene), 8.45 (d, ^3J = 8.0 Hz, 2H, perylene), 8.57 (brd, ^3J = 7.6 Hz, 2H, perylene); ^{13}C NMR ($CDCl_3$): δ = 14.03, 22.58, 26.97, 29.23, 31.76, 32.38, 54.91, 122.07, 122.80, 123.26, 125.90, 126.21, 127.78, 129.32, 131.40, 133.74, 134.91, 159.83; UV/Vis ($CHCl_3$): λ_{max} (ε) = 527 (80000), 491 (48600), 460 nm (17800); MS (70 eV): *m*/*z* (%): 588 (10), 587 (25) [M^+], 407 (14), 406 (53), 405 (100), 376 (22); elemental analysis calcd for $C_{37}H_{37}N_3O_4$ (587.7): C 75.61, H 6.35, N 7.15; found: C 75.32, H 6.24, N 7.01.

5a: Compound **2a** (110 mg, 0.19 mmol), **3a** (100 mg, 0.17 mmol), and imidazole (1 g) were heated under reflux with stirring (140 °C, 60 min). The reaction mixture was worked up as described for **3a** and purified by column separation (neutral Al_2O_3, $CHCl_3$/1-butanol (40/1) and then silica gel, $CHCl_3$/1-butanol (40/1)) to give **5a** (80 mg, 39%). R_f (silica gel, $CHCl_3$/1-butanol (40/1)) = 0.33; IR (KBr): $\tilde{\nu}$ = 2954 (m), 2927 (s), 2856 (m), 1735 (w), 1717 (s), 1698 (s), 1660 (s), 1594 (s), 1579 (s), 1457 (m), 1430 (m), 1404 (s), 1354 (m), 1334 (s), 1252 (s), 1204 (m), 1174 (m), 810 (s), 800 (m), 741 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ = 0.80 (t, 12H, 4 CH_3), 1.28 (m_c, 32H, 16 CH_2), 1.90 (m_c, 4H, 4 α-CH_2), 2.27 (m_c, 4H, 4 α-CH_2), 5.18 (m_c, 2H, 2 NCH), 8.22 (d, ^3J = 7.9 Hz, 4H, perylene), 8.38 (d, ^3J = 7.9 Hz, 4H, perylene), 8.45 (d, ^3J = 7.9 Hz, 4H, perylene), 8.61 (brs, 4H, perylene); ^{13}C NMR ($CDCl_3$): δ = 14.02, 22.58, 27.02, 29.21, 31.76, 32.36, 54.88, 122.21, 122.55, 123.56, 124.24 (br), 125.82, 126.09, 129.03, 129.40, 131.01 (br), 131.73 (br), 132.10, 133.43, 135.15, 159.98, 163.21 (br), 164.31 (br); UV/Vis ($CHCl_3$): λ_{max} (ε) = 535 (241800), 496 (97700), 462 nm (29600); fluorescence ($CHCl_3$): λ_{max} = 540, 581 nm; solid-state fluorescence: λ_{max} = 530, 637 nm; MS (70 eV): *m*/*z* (%): 1143 (0.8), 1142 (1.3) [M^+], 962 (1.3), 961 (2.7), 960 (1.2), 780 (1.7), 779 (5.4), 778 (6.3), 572 (0.9), 392 (1.8), 391 (8), 390 (14), 373 (2), 345 (1), 182 (52); elemental analysis calcd for $C_{74}H_{70}N_4O_8$ (1143.4): C 77.73, H 6.17, N 4.90; found: C 77.61, H 6.20, N 4.89.

6a: Compound **3a** (300 mg, 0.51 mol), **4** (100 mg, 0.26 mmol), zinc acetate dihydrate (60 mg, 0.26 mmol), and imidazole (2 g) were heated under reflux with stirring (150 °C, 3.5 h). The reaction mixture was worked up as described for **3a** and purified by column separation (neutral Al_2O_3, $CHCl_3$/ethanol (10/1) and then silica gel, toluene/acetic acid (15/1)). By-products were eluated first, and **6a** (60 mg, 15%) was collected by elution with $CHCl_3$/1-butanol (40/1); R_f (silica gel, $CHCl_3$/1-butanol (40/1)) = 0.34; IR (KBr): $\tilde{\nu}$ = 3065 (w), 2952 (m), 2927 (m), 2856 (m), 1738 (w), 1716 (brs), 1698 (brs), 1660 (s), 1593 (s), 1580 (m), 1428 (m), 1403 (m), 1353 (m), 1329 (s), 1252 (m), 1202 (m), 1126 (m), 965 (m), 852 (m), 810 (s), 796 (m), 738 (m), 725 (m), 663 cm^{-1} (m); ^1H NMR ($C_2D_2Cl_4$, 90 °C): δ = 0.87 (t, 12H, 4 CH_3), 1.29 (m_c, 32H, 16 CH_2), 1.95 (m_c, 4H, 4 α-CH_2), 2.27 (m_c, 4H, 4 α-CH_2) 5.16 (m_c, 2H, 2 NCH), 8.50 (m_c, 12H, perylene), 8.61 (d, ^3J = 7.8 Hz, 4H, perylene), 8.66 (d, ^3J = 7.5 Hz, 4H, perylene), 8.78 (d, ^3J = 8.0 Hz, 4H, perylene); UV/Vis ($CHCl_3$): λ_{max} (ε) = 538 (416900), 497 (135000), 463 nm (38500); fluorescence ($CHCl_3$): λ_{max} = 543, 583 nm; MS (FAB, 3-nitrobenzyl alcohol matrix): *m*/*z* (%): 1532 (0.1), 1531 (0.1), 1530 (0.1) [M^+], 1350 (0.6), 1349 (0.6), 1168 (0.4), 1167 (0.5), 1166 (0.2), 961 (0.4), 779 (3), 391 (24), 390 (14), 373 (18), 345 (14); the molecular mass of **6a** was verified by gel chromatography;[5] elemental analysis calcd for $C_{98}H_{78}N_6O_{12}$ (1531.7): C 76.85, H 5.13, N 5.49; found: C 75.91, H 5.04, N 5.67.

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p-Benzyne**

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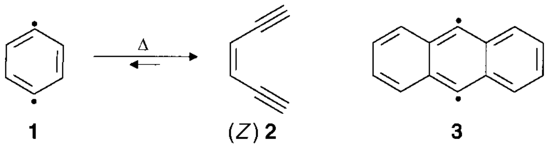
Elfi Kraka, Dieter Cremer,* and
J. George Radziszewski*

*Dedicated to Professor Dr. Günther Maier
on the occasion of his 66th birthday*

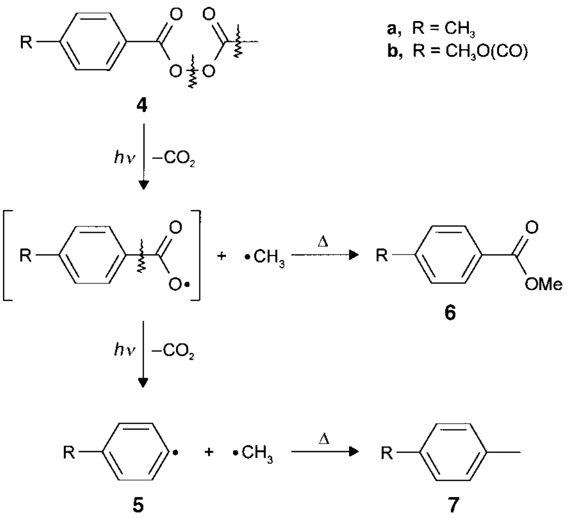
Since the discovery of the enediyne antibiotics there has been great interest in *p*-benzyne (1,4-didehydrobenzene, **1**) and its derivatives.[1–3] Compound **1** is formed as a reactive intermediate at very low stationary concentrations in the rearrangement of (*Z*)-3-hexene-1,5-diyne [(*Z*)-**2**],[4–6] and can be trapped in the gas phase with O_2 or NO.[7] Roth et al. determined the heat of formation of **1** from the kinetics of these trapping reactions to be 138.0 ± 1 kcal mol^{-1} (which means it is 8.5 kcal mol^{-1} less stable than (*Z*)-**2**), and the barrier toward ring opening to be 19.8 kcal mol^{-1}.[7]



1 (*Z*) **2** **3**

Although several attempts at the synthesis of **1** from *p*-substituted benzene derivatives are reported in the literature,[8, 9] the only derivative of **1** so far characterized spectroscopically, at low temperature, is 9,10-didehydroanthracene (**3**).[10] Squires et al. determined thermochemical data for **1** through collision-induced dissociation of the *p*-chlorophenyl anion in the gas phase in a quadrupole mass spectrometer.[11, 12] These data ($\Delta H_f^\circ = 137 \pm 3$ kcal mol^{-1}) are in excellent agreement with the values reported by Roth et al.[7] and with theoretical data from ab initio calculations at the CCSD(T)[13, 14] and CASSCF/CASPT2[15] levels of theory. Thus, both experiment and theory predict **1** to lie in an energy well sufficiently deep to permit, in principle, its isolation at low temperature. Here we report a matrix isolation and IR spectroscopic characterization of *p*-benzyne (**1**).

Acyl peroxides of type **4** were first used by Pacansky et al.[16, 17] for the matrix isolation of radicals, and were recently utilized for the generation of the phenyl radical[18] and the synthesis of *m*-benzyne.[17] Upon irradiation, **4** decomposes to an aryl radical **5**, CO_2, and a second radical, which in the case of acetyl peroxides is a methyl radical (Scheme 1). As long as the temperature of the matrix is kept low enough to prevent the diffusion of small molecules, the two radical fragments are separated by two CO_2 molecules, but at higher temperatures the radicals react rapidly to give **6** and **7**.



Scheme 1. Photolysis of **4a**, **b** in argon at 10 K.

Similarly, diacetylterephthaloyl diperoxide (**8**)[19] should yield **1**, CO_2, and methyl radicals (Scheme 2). Vacuum flash pyrolysis of **8** at temperatures between 300 and 600 °C and trapping of the products in argon at 10 K resulted in the formation of *Z* enediyne **2** and CO_2 as the main products, together with a small amount of dimethyl terephthalate (**6b**).

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