chromium (**5**) in essentially the same way as **4** → **7**: yield 80%; mp 143–144 °C; NMR (CDCl$_3$) $\delta$ 2.4–3.1 (3 H, m, C$_2$- and C$_3$-H), 3.2 (3 H, s, OCH$_3$), 3.5 (3 H, s, OCH$_3$), 4.15 (1 H, m, OH), 5.1–5.6 (4 H, m, aromatic protons); MS, $m/z$ 330 (M$^+$), 299, 274, 246, 228, 215, 198, 184 (100), 146, 132, 103, 52.

**(2,2-Dimethoxy-2-phenylethano)tricarbonylchromium (9).** ($\eta^6$-Acetophenone)tricarbonylchromium (**6**) was converted to $\alpha$-hydroxy dimethyl acetal **9** essentially the same way as **4** → **7**: yield 60%; mp 96–98 °C; NMR (CDCl$_3$) $\delta$ 2.1 (1 H, t, OH), 3.3 (6 H, s, O CH$_3$'s), 3.7 (2 H, d, CH$_2$), 5.0–5.8 (5 H, m, aromatic protons); MS, $m/z$ 318 (M$^+$), 287, 262, 234, 203, 202, 186, 172 (100), 133, 114, 103, 100, 91, 52.

**[(−)-1,1-Dimethoxy-2-tetralol]tricarbonylchromium [(2*R*)-7].** This reaction was carried out as above: mp 154–157 °C; yield 80%; $[\alpha]^{24}_{D}$ −44° ($c$ 0.058, CHCl$_3$); IR (KBr, cm$^{-1}$) 3500 (OH str), 1960, 1880, 1865 (C≡O).

**1,1-Dimethyl-2-tetralol (10).** (1,1-Dimethoxy-2-tetralol)tricarbonylchromium (**7**; 70 mg, 0.0002 mol) was dissolved in anhydrous ether (200 mL) and was kept in sunlight for 6 h. The reaction mixture was filtered, and filtrate was washed with water (2 × 30 mL) and dried over anhydrous MgSO$_4$. After filtration it was concentrated in vacuo. The white semisolid product thus obtained was treated with hexane to obtain a white crystalline solid: 37 mg (90%); mp 93–94 °C; IR (CHCl$_3$ cm$^{-1}$) 3450 (OH str); NMR (CDCl$_3$) $\delta$ 2.0–2.9 (4 H, m, CH$_2$'s), 3.03 (3 H, s, OCH$_3$), 3.35 (3 H, s, OCH$_3$), 4.2 (1 H, m, C$_2$-H), 7.0–7.8 (4 H, m, aromatic protons).

**(−)-1,1-Dimethoxy-2-tetralol [(2*R*)-10].** This reaction was done as above: mp 91 °C; yield 80%; $[\alpha]^{24}_{D}$ −40° ($c$ 0.096, CHCl$_3$).

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**Registry No.** 1, 529-34-0; 4, 32735-36-7; (+)-4, 12110-42-8; 5, 12153-72-9; 6, 12153-11-6; 7, 105561-11-3; (2*R*)-(−)-7, 103421-50-7; 8, 105561-12-4; 9, 103371-68-2; 10, 83022-55-3; (2*R*)-(−)-10, 103239-03-8; Cr(CO)$_6$, 13007-92-6.

**Supplementary Material Available:** Table of X-ray positional parameters and temperature factors for **7** (2 pages). Ordering information is given on any current masthead page.

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# Charge-Transfer and Exciplex Pathway in the Photocycloaddition of 9-Anthracenecarbonitrile with Anthracene and Naphthalenes

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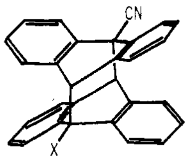
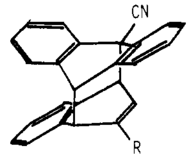
The role of excited complexes and of charge-transfer interaction in the 4 + 4 photocycloaddition of aromatic molecules is a subject of current interest.[1,2] Recent flash photolysis evidence suggests that the intermediate in the photocycloaddition (and photocycloreversion) of linked anthracenes has ion pair character in acetonitrile but not in diethyl ether.[3] From the preparative point of view it is known that an increase in the polarity of the medium enhances the yield of cross dimerization between 9-anthracenecarbonitrile (ACN) and 9,10-dimethylanthracene[4] and that the medium influences the head-to-head/head-to-tail ratio in the dimerization of 9-substituted anthracenes.[5] The formation of a head-to-head cross dimer from 9-methoxyanthracene and ACN is due to charge-transfer interaction.[6]

Chart I



1, X = CN
4, X = H



2, R = H
3, R = Me

We presently report the cross photodimerization of ACN with other aromatic molecules. The aim of the present study was twofold, viz. (i) to obtain mechanistic information by comparing the results with donors of different ionization potential and in different solvents, and (ii) to exploit charge-transfer excited complexes for the synthesis of new cross dimers, in particular anthracene–naphthalene 4 + 4 adducts, as these were previously obtained only by intramolecular cycloaddition from bichromophoric compounds.[1a,7]

## Results and Discussion

Degassed solutions (2 × 10$^{-3}$ M) of ACN in cyclohexane or acetonitrile were irradiated in the presence of aromatic donors at a concentration high enough to ensure that a significant portion of ACN singlet excited state is quenched. In the absence of quenchers ACN reacts efficiently under these conditions to yield the 4 + 4 dimer **1**[8] (Chart I), which precipitates out during irradiation.

Naphthalene is a poor quencher of ACN fluorescence (Table I, Stern–Volmer constant from steady-state measurements, $K_{SV} \leq 1.5$ M$^{-1}$). Irradiation in the presence of 0.05 M naphthalene yields an abundant precipitate of dimer **1**, but a new product is present in solution and is obtained in satisfactorily pure state by chromatography and recrystallization despite its limited stability (Table I). Spectroscopic properties (see Experimental Section) as well as reversion to ACN and naphthalene on melting or at room temperature both in solution (in days) or in the crystalline state (in months) allow unambiguous recognition of this compound as the cross dimer **2**.

Both 1- and 2-methylnaphthalene are better quenchers of ACN fluorescence than unsubstituted naphthalene. In the presence of the former compound the only product obtained is dimer **1**, but in the latter case this is accompanied by a certain amount of the cross dimer **3**, similar to product **2** as far as properties and stability are concerned.

This fits with the idea that substituents in position 1 hinder photocycloaddition and led to the examination of more 2-substituted naphthalenes. Compounds with electron-withdrawing substituents such as 2-cyano- or 2-carbomethoxynaphthalene do not appreciably quench ACN fluorescence nor influence dimerization to **1**.

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**Table I. Photochemical Reaction between 9-Anthracenecarbonitrile and Various Donors**

| donor | solvent | $K_{SV}$, $M^{-1}$ | $[D]^a$ | products (% yield) | $\Phi_{lim}{}^b$ |
|---|---|---|---|---|---|
| naphthalene | cyclohexane | low | 0.05 | **1** (37), **2** (10) | 0.03 |
| | MeCN | 1.5 | 0.05 | **1** (33), **2** (38) | 0.06 |
| 1-methylnaphthalene | cyclohexane | 3 | 0.05 | **1** (65) | |
| | MeCN | 13 | 0.05 | **1** (75) | |
| 2-methylnaphthalene | cyclohexane | 3 | 0.05 | **1** (26), **3**(25) | |
| | MeCN | 13 | 0.05 | **1** (26), **3** (38) | |
| 2-methoxynaphthalene | cyclohexane | 79 | 0.007 | **1** (45) | |
| | MeCN | 166 | 0.007 | **1** (40) | |
| 2-cyanonaphthalene | cyclohexane | low | 0.01 | **1** (65) | |
| | MeCN | low | 0.01 | **1** (70) | |
| anthracene | cyclohexane | 255 | 0.003 | **4** (94) | 0.13 |
| | MeCN | 280 | 0.003 | **4** (91) | 0.45 |

[a] Donor concentration in preparative experiments. [b] Limiting quantum yield for cross dimerization at infinite donor concentration, from eq 2.

The good donor 2-methoxynaphthalene efficiently quenches the ACN excited singlet state and originates a weak exciplex emission in cyclohexane ($\lambda_{max}$ 480 nm). From the photochemical point of view, 2-methoxynaphthalene slows down the dimerization of ACN to yield product **1**, but no cross dimer is formed.

Several other hydrocarbons were tested. Indene and phenanthrene do not yield any cross dimer with ACN. Anthracene is an efficient quencher of ACN fluorescence, $k_q$ reaching the diffusion controlled limit. In the presence of $3 \times 10^{-3}$ M anthracene dimerization of ACN to **1** is virtually suppressed, and a new product, easily recognized as the cross dimer **4**, is obtained in high yield. Product **4** is much more stable in the crystalline state and in solution than the anthracene–naphthalene adducts **2** and **3**. Calorimetric measurements show that compound **4** undergoes exothermic dedimerization on heating the crystals below the melting point, analogously to what has been reported for compound **1**.[9,10]

Quantum yield for cross dimer formation was measured in separated experiments with a lower ($2 \times 10^{-4}$ M) ACN concentration. Limiting quantum yields at infinite donor concentration (Table I) were evaluated from the linear double reciprocal plot of quantum yield vs. quencher concentration (see below).

The present results can be rationalized with reference to Scheme I, which considers the intermediacy of an exciplex with partial charge transfer character. This evolves by emission, separation into solvated radical ions or adduct formation. Quantum yield of reaction is

$$\Phi = \frac{k_r}{k_r + k_d' + k_d''} \cdot \frac{k_q[D]}{k_q[D] + k_d} \qquad (1)$$

or in the inverse form

$$\Phi^{-1} = \frac{k_d + k_d' + k_d''}{k_r}\left(1 + \frac{k_d}{k_q}[D]^{-1}\right) \qquad (2)$$

Cross dimerization clearly involves ACN singlet excited state, as shown inter alia by the correspondence between the $k_q/k_d$ value obtained from fluorescence quenching measurements ($K_{SV} = k_q/k_d$) and from the dependence of reaction quantum yield on the donor concentration (in eq 2, intercept/slope = $k_q/k_d$).

In a polar solvent both $k_q$ and $\Phi_{lim} = k_r/k_d' + k_d'' + k_r$ are increased. In the reaction of ACN with anthracene, $k_q = k_{diff}$ already in cyclohexane, but an increase of $\Phi_{lim}$ in acetonitrile is observed. Thus, acetonitrile favors cycloaddition through a significantly polar intermediate. Partitioning from the exciplex is much less favorable to cycloaddition in the case of ACN–naphthalene complexes ($k_r/\sum k$ = 0.03–0.06) than in the case of ACN–anthracene complex ($k_r/\sum k$ = 0.13–0.45).

The correlation diagram for photochemically allowed cycloaddition[11] is more tilted in the former case than in the latter as the products are higher in energy. Thus, in the case of the reaction between ACN and naphthalenes only a shallow minimum corresponds to the exciplex configuration in the singly excited surface and access to the pericyclic minimum (corresponding to the avoided crossing between surfaces connecting double excited and ground state) is difficult. In the case of the reaction between ACN and anthracene and, in general, of anthracenes photodimerization, the singly excited surface is not so steep and access both to the exciplex and to the pericyclic minimum is easier. In the former case steric hindering by substituents at the position where the bonding occurs is much more effective. ACN does not react with 1-methylnaphthalene, whereas it does react with 9-methyl- or 9,10-dimethylanthracene.[4] Furthermore, lowering the energy of the exciplex, as in the reaction with 2-methoxynaphthalene, obviously enhances $k_q$ but has no beneficial effect on $k_r$, since the barrier toward reaction increases as the minimum corresponding to the exciplex becomes deeper. Thus the other modes of decay from the exciplex, viz., emission ($k_d'$) and unproductive radical ion separation ($k_d''$) predominate. Literature data show that this is not the case for cross dimerization between anthracenes. There, compounds with different ionization potential, forming a polar exciplex, photodimerize efficiently.[6]

In conclusion it appears that cross dimerization of ACN with naphthalenes and anthracene takes place through a significantly polar intermediate and is moderately affected by solvents and substituents. More determining are energetic factors which make anthracene–naphthalene cross dimers less attainable, and this situation is not overcome by charge-transfer interaction. Thus, cross dimerization of unlinked anthracenes and naphthalenes is possible as shown in the present paper but is limited in scope.

## Experimental Section

Commercial samples of aromatic compounds were purified by chromatography and recrystallization. New products gave satisfactory elemental analysis (C, H, N).

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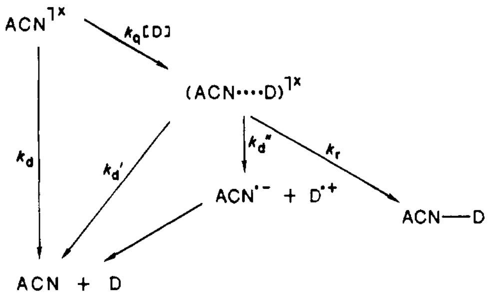
**Scheme I**



**Photochemical Reactions.** A solution of 9-anthracenecarbonitrile (ACN, 200 mg) and naphthalene (2 g) in 300 mL acetonitrile was deaerated by boiling and cooling while flushing with argon and irradiated at 17 °C by means of a high-pressure mercury arc (Philips HPK 125 W) through Pyrex for 30 min. Evaporation of the solvent and chromatography on a silica gel column, eluting with cyclohexane–ethyl acetate mixture yielded 10 mg of unreacted ACN, 63 mg (33%) of 9-anthracenecarbonitrile homodimer (1), and 118 mg (38%) of 9-cyano-9,10,11,14-tetrahydro-9,10-[1,4]naphthalenoanthracene (2), colorless crystals from hexane, which decomposes on rapid heating at ca. 135 °C: NMR $\delta$ 3.35 (11-H, ddd), 3.95 (10-H, d), 4.2 (14-H, dd), 5.75 m (12-H, 13-H) [$J_{11-12} = 11$ Hz, $J_{12-14} = 2$ Hz, $J_{13-14} = 6$ Hz); IR 2235 cm$^{-1}$. Crystals of this compound become visibly yellow after several days, and the presence of ACN and napthalene can then be detected. The other photoreactions were carried out as reported in Table I. New photoproducts are the following. 9-Cyano-12-methyl-9,10,11,14-tetrahydro-9,10-[1′,4′]naphthalenoanthracene (3), colorless crystals from hexane (decomposes on rapid heating at ca. 130 °C): NMR $\delta$ 3.2 (11-H, d), 3.9 (10-H, d), 4.15 (14-H, d), 5.35 (13-H, d) [$J_{10-11} = 10.5$ Hz, $J_{13-14} = 7.5$ Hz]; IR 2235 cm$^{-1}$. 9-Cyano-9,10,11,16-tetrahydro-9,10-[9′,10′]anthracenoanthracene (4), colorless crystals from cyclohexane: mp 154–155 °C on rapid heating (with decomposition); NMR $\delta$ 4.05 (10-H, 11-H, s), 4.9 (16-H, s); IR 2239 cm$^{-1}$.

**Fluorescence Quenching.** Fluorescence measurements were carried out on solutions degassed by five freeze–degas–thaw cycles by means of an Aminco Bowman MPF spectrophotofluorimeter linear Stern–Volmer plots were obtained in every case.

**Reaction Quantum Yield.** Reaction quantum yield was measured at 366 nm on ACN solutions ($2 \times 10^{-4}$ M) degassed by five freeze–degas–thaw cycles on a optical bench fitted with a super-high-pressure mercury arc (Osram 200 W/2). Light was collimated by means of quartz lenses and monochromatized by means of an interference filter. Light flux ($10^{-7}$ einstein min$^{-1}$ cm$^{-2}$) was measured by ferrioxalate actinometry.

**Acknowledgment.** This work was supported by CNR, Progetto Finalizzato Chimica Fine e Secondaria.

**Registry No.** 1, 33998-38-8; 2, 105598-00-3; 3, 105597-98-6; 4, 105597-99-7; 9-anthracenecarbonitrile, 1210-12-4; naphthalene, 91-20-3; 2-methylnaphthalene, 91-57-6; anthracene, 120-12-7; 1-methylnaphthalene, 90-12-0; 2-cyanonaphthalene, 613-46-7; 2-methoxynaphthalene, 93-04-9.

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# Synthesis and Reactivity of New Pentacoordinated Phosphoenolpyruvate Derivatives

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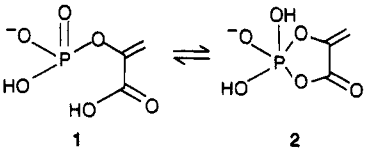
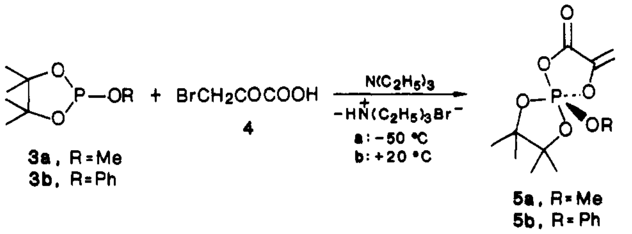
Pentaoxyphosphoranes are thought to be closely related intermediates to the biologically important phosphate ester reactions.[1,2] Thus, the hydrolysis of phosphoenolpyruvate 1, a strong phosphorylating agent,[3,4] proceeds most probably via the formation of the cyclic acyloxyphosphorane[5] 2 (eq 1).



(1)

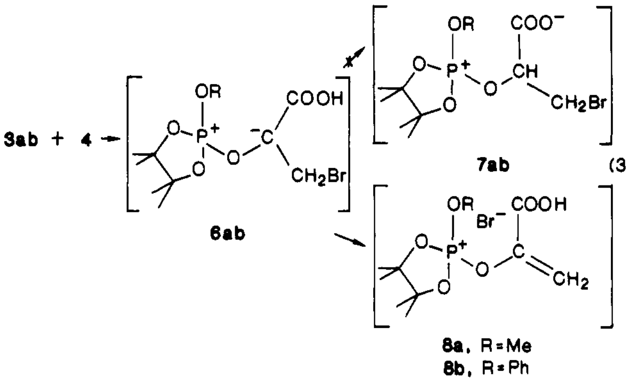
To our knowledge, structures of type 2 have not yet been isolated. So, it becomes important to prepare well-defined species having a structure as close as possible of the structure of 2.

The synthesis (eq 2) involves the first step of a Perkow reaction followed by a ring closure. Since no reaction



(2)

occurs at room temperature between **3a** or **3b** and an equivalent amount of triethylammonium bromopyruvate, the first step is probably the attack of the phosphite **3** on the acid **4**. This step proceeds without any proton transfer, as observed with $\alpha$-keto acids,[6] in the phosphonium oxyanions **6a** and **6b** (eq 3). Moreover, despite the elimination of Br$^-$, no Arbuzov reaction takes place in the case of **8a** (R = Me), although it is the major reaction with trimethyl phosphite.[3a] However, the presence of the dioxaphospholane ring in **3** facilitates the ring closure[6] of **8** to give the spirophosphoranes[7] **5**.



(3)

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