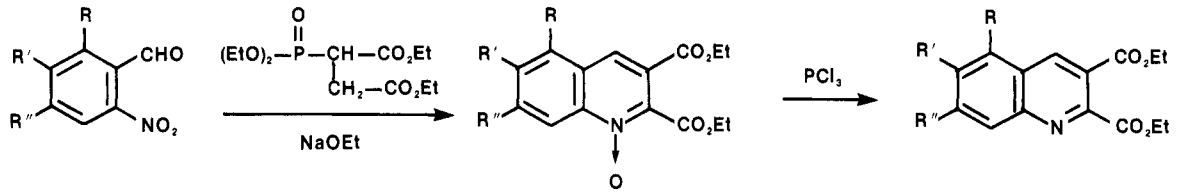
Scheme I



1 2 3

	R	R′	R″
a	H	H	H
b	Cl	H	H
c	H	Cl	H
d	H	F	H
e	H	OCH_3	OCH_3
f	H	$-O-CH_2-O-$	

Table I. Melting Points, Solvents of Recrystallization, and Yields of Quinoline *N*-Oxides[a] 2 and Quinolines[a] 3

compd	mp, °C	solvent of recrystalln	yield, %
2a	111–112	$CHCl_3$/IPE[b]	40
2b	95–96	IPE[b]	45
2c	120.5–121.5	IPO[c]	47
2d	84–85	IPE[b]	50
2e	214–215	CH_3CN	71
2f	174.5–175.5	C_2H_5OH	39
3a	54–55[d]	hexane	61
3b	42.5–43.5	PE[e]	59
3c	93–94	IPE[b]	47
3d	55.5–56.5	PE[e]	72
3e	131.5–132.5	IPO[c]	62
3f	132.5–133.5	IPO[c]	73

[a] All analyses are within ±0.3% of calculated values. [b] Isopropyl ether. [c] 2-Propanol. [d] Reported mp 55 °C (see ref 7). [e] Petroleum ether.

(0.027 mol) in 5 mL of ethanol. The resulting dark solution was stirred for 1.5 h while maintaining the reaction mixture in an ice bath. The solvent was evaporated under reduced pressure and the residue partitioned between ethyl acetate and water. The ethyl acetate was dried over Na_2SO_4 and then evaporated under reduced pressure. The residue was recrystallized from chloroform–isopropyl ether.

Compounds **2b–f** were prepared by the same procedure, following the course of the reactions by thin-layer chromatography. In the preparation of compounds **2b**, **2e**, and **2f**, small amounts of dimethylformamide were used to aid in dissolution of the starting aldehydes. For compounds **2b** and **2d**, purification was carried out by chromatography over silica gel, using $CHCl_3$ as eluent.

Compound **2a** also was synthesized by heating on the steam bath a solution of 0.27 g (0.001 mol) of diethyl quinoline-2,3-dicarboxylate[7] and 0.43 mL of 30% H_2O_2 in 0.5 mL of acetic acid for 3.5 h. The reaction mixture was poured into 20 mL of saturated $NaHCO_3$ and the precipitate obtained was filtered, dried, and recrystallized from isopropyl ether, mp 111–112 °C. Both infrared and NMR spectra were superimposable on those of **2a** prepared according to the above procedure.

Diethyl Quinoline-2,3-dicarboxylate (3a).[7] A solution of 0.87 g (0.003 mol) of **2a** and 1.24 g (0.009 mol) of PCl_3 in 40 mL of $CHCl_3$ was refluxed for 3 h. Solvent was removed under reduced pressure and the residue was partitioned between ethyl acetate and water. The organic layer was dried over Na_2SO_4, and, following evaporation, the residue was recrystallized from petroleum ether.

Compounds **3a–f** were prepared similarly except that compound **3b** was purified by chromatography over silica gel, using $CHCl_3$ as eluent.

Registry No. **1a**, 552-89-6; **1b**, 6361-22-4; 1c, 6628-86-0; **1d**, 395-81-3; **1e**, 20357-25-9; **1f**, 712-97-0; **2a**, 92525-68-3; **2b**, 92641-44-6; **2c**, 92525-69-4; **2d**, 92525-70-7; **2e**, 92525-71-8; **2f**, 92525-72-9; **3a**, 32413-08-4; **3b**, 92525-73-0; **3c**, 92525-74-1; **3d**, 92525-75-2; **3e**, 92525-76-3; **3f**, 92525-77-4; diethyl (diethoxyphosphinyl)succinate, 7071-15-0.

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Access to the 3,5,6,7-Tetrahydro-2*H*-1-benzopyran Ring System from 2,3,5,6,7,8-Hexahydrobenzo-4*H*-pyran-4-one Derivatives

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The hydride reduction of the cyclohexenone system has been a subject of numerous studies.[1] In contrast, only one study was made on 2,2,6-trimethyl-2,3-dihydro-4*H*-pyran-4-one.[2] It is therefore considered interesting to carry out experimental studies on 2,3,5,6,7,8-hexahydrobenzo-4*H*-pyran-4-one derivatives[3,4] in order to evaluate the directive effect of the oxygen atom.

Reduction of the hexahydrobenzopyran-4-ones **1a–d** with lithium aluminum hydride proceeded rapidly to afford the allylic alcohols **2a–d**. However, they underwent rapid polymerization to form a polymeric material at room temperature for 1 day. The reaction appeared stereoselective since only the cis 4-hydroxy-2-methyl isomers were otained in the case of **2b** and **2d**. These results require that the addition of the hydride ion occurs from the same side of the molecule as the axial hydrogen at C-2 in a half-chair conformation as in 5-substituted cyclohexenones.[1] Structure **2** was based on standard spectroscopic methods. The configurations of **2b** and **2d** were

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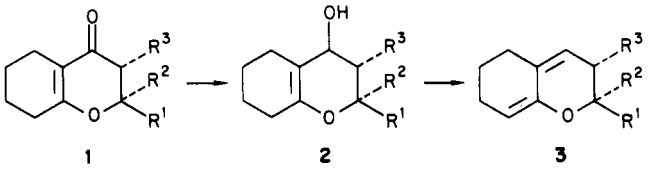
deduced from 350-MHz ^1H NMR spectra by decoupling experiments. The vicinal C-4/C-3 protons have a pseudoaxial/axial relationship, in a half-chair conformation, as evidenced by the coupling constant of 9 Hz. The value of $J_{H\text{-}2,H\text{-}3}$ = 10–11 Hz allowed us to assert the pseudoequatorial position of the 2-methyl. These values are in good agreement with those found in flavan-4-ols,[5-7] chroman-4-ols,[8] and 2-cyclohexenols.[9]

Upon gas chromatography, the alcohols **2** were dehydrated to afford only the hitherto unknown dienes **3**.



1 **2** **3**

a, $R^1 = R^2 = R^3 = H$
b, $R^1 = Me$; $R^2 = R^3 = H$
c, $R^1 = R^2 = Me$; $R^3 = H$
d, $R^1 = R^3 = Me$; $R^2 = H$

Conversion to **3** was also easily performed, in a preparative scale, upon heating **2** on Chromosorb W at 230 °C. All attempts of acid-catalyzed dehydration of **2** afforded a polymeric material. The mechanism of dehydration is not obvious since β-hydrogen abstraction at C-3 could be followed by double-bond isomerization; δ-hydrogen abstraction at C-8 was also possible.

The spectral assignments in the 350-MHz ^1H NMR spectra were made by decoupling experiments and coupling constant data. The assignment of the olefinic resonance at C-4 was ensured by specific deuteration using lithium deuterioaluminum hydride. On irradiation of the H-4, the signal of the H-8 changed to a triplet, $J_{H\text{-}8,H\text{-}7} = J_{H\text{-}8,H\text{-}7'}$ = 4 Hz. irradiation of the H-3 and H-7 protons caused the pattern for H-8 to simplify to a doublet, $J_{H\text{-}4,H\text{-}8}$ = 2 Hz, characteristic of a planar zigzag orientation;[10] a narrow unresolved signal with a half-bandwidth of 3.5 Hz appeared for the H-4. The H-8 proton signals occurred at higher field (δ 5.09–5.13) than the H-4 (5.27–5.55) and were well resolved. The H-4 proton resonances gave broad ill-defined envelope stretchings, probably due to the fact that it was not only coupled with H-3 and H-8 but also allylically coupled to two H-5 in rapid interconversion. In the case of a double bond located in the 3,4-position, the value $J_{H\text{-}3,H\text{-}4}$ would be ≃10 Hz.[11,12] In addition, the shift of the 3-methyl (**3d**) at δ 0.96 clearly is indicative that it is attached to a sp^3 carbon. The UV data, λ_{max} 250 nm, corroborate the transoid diene structure, the wavelength maxima of a cisoid diene would be 275–280 nm.[13] These compounds polymerized very readily and therefore were handled and stored under nitrogen.

Values for thermochemical properties of hexahydronaphthalenes and tetrahydrobenzopyrans have been estimated.[14] 1,2,3,5,6,7-Hexahydronaphthalene was found the most stable. Therefore, by analogy, the most stable unsubstituted tetrahydro-1-benzopyran was predicted as having its double bonds located as in 1,2,3,5,9,7-hexahydronaphthalene. Our results are of interest since we have substantiated this suggestion. The transoid dienic structure (3,5,6,7-tetrahydro-2*H*-1-benzopyran system) was exclusively produced regardless of whether substituents are present or not on the pyran ring.

Experimental Section

Melting points were determined on a Kofler block. Infrared and ultraviolet spectra were obtained with Beckman Model Acculab 2 and DB spectrometers. ^1H NMR spectra were recorded by using Brucker WP-80 80-MHz or 350-MHz Cameca spectrometers and are expressed in parts per million from Me_4Si. New compounds have satisfactory C, H analyses (Microanalytical Laboratory, Centre National de la Recherche Scientifique, 69390 Vernaison, France) which were submitted for review.

Compounds **1** were prepared as previously described.[3,4]

General Preparation of 3,4,5,6,7,8-Hexahydro-2*H*-1-benzopyran-4-ols 2a–d. To a suspension of $LiAlH_4$ (1 g, 26 mmol) in anhydrous ether (15 mL) cooled to 0° C was added dropwise a solution of **1** (10 mmol) in anhydrous ether (15 mL). The mixture was stirred for an additional hour while it attained room temperature. The excess of $LiAlH_4$ was decomposed by adding 2 mL of water and 1.6 mL of 10% aqueous sodium hydroxide. The mixture was stirred until the salts became granular, then it was filtered. The ether solution was dried (Na_2SO_4), the solvent was removed, and the residue was purified by column chromatography [SiO_2, ethyl ether].

3,4,5,6,7,8-Hexahydro-2*H*-1-benzopyran-4-ol (2a): 80% yield, oil; IR (liquid film) 3500–3300, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.50 (m, 11 H, with 1 H D_2O exchangeable), 3.50–4.10 (m, 3 H). Anal. ($C_9H_{14}O_2$) C, H.

***cis*-2-Methyl-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-4-ol (2b)**: 80% yield; mp 58–59 °C (hexane); IR (Nujol) 3500–3300, 1685 cm^{-1}; ^1H NMR (350 MHz, $CDCl_3$) δ 1.28 (d, J = 6 Hz, 3 H), 1.40–2.30 (m, 11 H, with 1 H D_2O exchangeable), 3.98 (m, decoupled by irradiation at 1.28, $J_{H\text{-}2,H\text{-}3}$ = 11 Hz, $J_{H\text{-}2,H\text{-}3'}$ = 2 Hz, 1 H-2), 4.24 (dd J = 9 and 7 Hz). Anal. ($C_{10}H_{16}O_2$) C, H.

2,2-Dimethyl-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-4-ol (2c): 85% yield; oil; IR (liquid film) 3500–3300, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3 H), 1.31 (s, 3 H), 1.50–2.50 (m, 11 H, with 1 H D_2O exchangeable), 4.05 (m, 1 H). Anal. ($C_{11}H_{18}O_2$) C, H.

***r*-2,*t*-3-Dimethyl-3,4,5,6,7,8-hexahydro-2*H*-1-benzopyran-*c*-4-ol (2d)**: 75% yield; mp 89–90 °C (hexane); IR (Nujol) 3500–3300, 1690 cm^{-1}; ^1H NMR (350 MHz, $CDCl_3$) δ 1.02 (d, J = 7 Hz, CH_3 C-3), 1.26 (d, J = 6 Hz, CH_3 C-2), 1.35–2.30 (m, 10 H, with 1 H D_2O exchangeable), 3.62 (qd, decoupled by irradiation at 1.26, $J_{H\text{-}2,H\text{-}3}$ = 10 Hz, 1 H-2), 3.66 (d, J = 9 Hz, 1 H-4). Anal. ($C_{11}H_{18}O_2$) C, H.

General Preparation of 3,5,6,7-Tetrahydro-2*H*-1-benzopyrans 3a–d. Chromosorb W (60–80 mesh; 2 g) was impregnated with a solution of **2** (10 mmol) in ether (20 mL). After evaporation of the solvent, the residual material was placed in a U tube which was kept heated in a furnace at 230 °C for 30 min, under a nitrogen atmosphere. After cooling the Chromosorb was extracted with ether, the solvent evaporated, and then the residue distilled under reduced pressure to afford the title compounds.

3,5,6,7-Tetrahydro-2*H*-1-benzopyran (3a): bp 68–70 °C (0.5 mmHg); 58% yield; UV (EtOH) λ_{max} (ε) 230 (9470), 249 (9360); ^1H NMR (350 MHz, $CDCl_3$) δ 1.64 (m 2 H-6), 2.15–2.25 (m, 2 H-3 and 2 H-7), 2.31 (m, 2 H-5), 3.93 (t, J = 5.5 Hz, 2 H-2), 5.09 (td, decoupled by irradiation, J = 4 and 2 Hz, 1 H-8), 5.55 (br, $w_{1,2}$ = 10 Hz, 1 H-4). Anal. ($C_9H_{12}O$) C, H.

2-Methyl-3,5,6,7-tetrahydro-2*H*-1-benzopyran (3b): bp 68–70 °C (0.5 mmHg); 50% yield; UV (EtOH) λ_{max} nm (ε) 229 (7700), 250 (9000); ^1H NMR (350 MHz), $CDCl_3$ δ 1.28 (d, J = 6.3 Hz, CH_3), 1.65 (m, 2 H-6), 2.13 (m, 2 H-3 and 2 H-7), 2.31 (m, 2 H-5), 3.89 (qdd, J = 6.3, 7.7 and 5.6 Hz, (1 H-2), 5.12 (td, J = 4 and 2 Hz, 1 H-8), 5.48 (br, $w_{1/2}$ = 10 Hz, 1 H-4). Anal. ($C_{10}H_{14}O$) C, H.

2,2-Dimethyl-3,5,6,7-tetrahydro-2*H*-1-benzopyran (3c): bp 68–70 °C (0.5 mmHg), UV (EtOH) λ_{max} nm (ε) 230 (8210), 250

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(9440); ^{1}H NMR (350 MHz, $CDCl_3$) δ 1.24 (s, 6 H, CH_3), 1.65 (m, 2 H-6), 2.15 (m, 2 H-3 and 2 H-7), 2.32 (m, 2 H-5), 5.12 (td, J = 4 and 2 Hz, 1 H-8); 5.38 (br, $w_{1/2}$ = 10 Hz, 1 H-4). Anal. ($C_{11}H_{16}O$) C, H.

***trans*-2,3-Dimethyl-3,5,6,7-tetrahydro-2*H*-1-benzopyran (3d)**: bp 68–70 °C (0.5 mmHg); UV (EtOH) λ_{max} nm (ϵ) 229 (9200), 250 (8200); ^{1}H NMR (350 MHz, $CDCl_3$) δ 0.96 (d, J = 7 Hz, CH_3 C-3), 1.28 (d, J = 6.3 Hz, CH_3 C-2), 1.65 (m, 2 H-6), 2.17 (m, 1 H-3 and 2 H-7), 2.32 (m, 2 H-5), 3.44 (qd, J = 6.3 and 9 Hz, 1 H-2), 5.13 (td, J = 4 and 2 Hz, 1 H-8), 5.27 (br, $w_{1/2}$ = 5.6 Hz, 1 H-4). Anal. ($C_{11}H_{16}O$) C, H.

[4-^{2}H]-2-Methyl-3,5,6,7-tetrahydro-2*H*-1-benzopyran (3b-[4-^{2}H]). This compound was obtained as described above using $LiAlD_4$ in an overall yield from **1b** of 40%: ^{1}H NMR ($CDCl_3$) δ 1.28 (d, J = 6 Hz, CH_3) 1.50–1.75 (m, 2 H-6), 2.0–2.4 (m, 2 H-3, 2 H-5 and 2 H-7), 3.90 (m, 1 H-2), 5.12 (t, J = 4 Hz, 1 H-8).

Registry No. **1a**, 29798-89-8; **1b**, 13738-56-2; **1c**, 29798-90-1; **1d**, 29767-23-5; **2a**, 92545-32-9; **2b**, 92545-33-0; **2c**, 92545-34-1; **2d**, 92545-35-2; **3a**, 62691-02-5; **3b**, 92545-36-3; **3b**-[4-^{2}H], 92545-39-6; **3c**, 92545-37-4; **3d**, 92545-38-5.

11,11,12,12-Tetracyanoanthraquinodimethane

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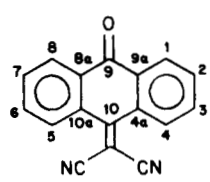
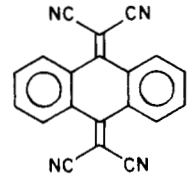
While the majority of sterically congested anthraquinones such as 1,4-, 1,5-, or 1,8-disubstituted anthraquinones display only minor structural deformations (e.g., longer bond lengths, wider bond angles, etc.) and remain relatively planar in structure,[1] 10-(dicyanomethylene)-anthrone **1** is a highly distorted molecule.[2] Structurally,



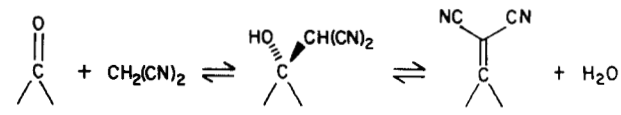
1



2

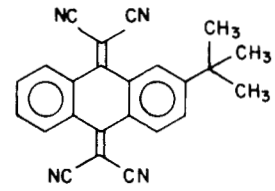
1 exists in a butterfly-like conformation with the two benzo moieties buckling in one direction while the central quinonoid ring adopts a boat conformation with its extremities pointing in the other direction.[3] The carbonyl and dicyanomethylidene functions are respectively bent by 11° and 36.5° from the plane described by C_{4a}–C_{9a}–C_{8a}–C_{10a}. Even with these distortions, the distance between the cyano carbon and C_4 or C_5 is still 2.84 Å, which is shorter than the value of 3.0 Å for non-bonded interactions of this type.[3] In light of this, we expect 11,11,12,12-tetracyanoanthraquinodimethane (**2**) to be an excessively overcrowded and severely deformed molecule. We describe here a facile synthesis and some molecular properties of this structurally interesting compound.[4]

Scheme I

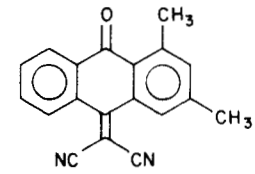


3

Although malononitrile generally condenses with aromatic carbonyl compounds with great ease,[5-7] its condensation with anthraquinone, however, cannot be executed under standard conditions. the excessive overcrowding in **2** obviously shifts the equilibrium of condensation in favor of the reactants and precludes the otherwise simple condensation (Scheme I). This difficulty, however, may be overcome if the tetrahedral intermediate **3** of the condensation could be forced to liberate water in an irreversible manner. We found that the Lewis acid $TiCl_4$ was an effective agent for promoting the condensation in the following manner: first, it activated the carbonyl functions of anthraquinone for condensation through complexation; second, it removed water from **3** irreversibly. Thus, when a mixture of anthraquinone and malononitrile was treated with excess $TiCl_4$ and pyridine as a base at room temperature for several hours, **2** was obtained in good yield. Similarly, 2-*tert*-butylanthraquinone condensed readily with malononitrile to afford 11,11,12,12-tetracyano-2-*tert*-butylanthraquinodimethane (**4**) under the same conditions. This method of condensation was in fact so effective that the monosubstituted species **1** could not be isolated under the reaction conditions. To obtain the monosubstituted species under these conditions, we found it necessary to introduce a blocking group into the antraquinone structure to prevent the second condensation. Accordingly, when 1,3-dimethylanthraquinone was subjected to the same reaction conditions, only 1,3-dimethyl-10-(dicyanomethylene)anthrone (**5**) was formed exclusively.



4



5

In structural analogy to **1**, **2** should have a butterfly-like conformation. The degree of deformation in **2**, however, should be far more severe than that in **1**. The electron affinity[8] of **2** was measured to be 2.21 eV, which is significantly lower than the value of ~2.45 eV expected for a planar structure of this molecule.[9] Apparently, the buckling of the benzo moieties and the severe out-of-plane distortion of the two dicyanomethylidene functions have deprived the latter, to a great extent, of the conjugation between them. In addition, despite its reasonably high electron affinity, **2** failed to form charge-transfer complexes even with strong electron donors such as tetrathiafulvalene (TTF). This anomalous behavior is to be expected if **2**

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(8) Electron affinity (EA) was determined from half-wave reduction potential ($E_{1/2}$) according to the equation EA = $-E_{1/2}$ + 2.49 (eV); see: Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183. Cyclic voltammetry was carried out in CH_2Cl_2 with tetrabutylammonium perchlorate as supporting electrolyte and Ag/AgCl. KCl as reference electrode.
(9) If **2** were a planar molecule, the difference between its EA and that of anthraquinone should be approximately the same as that between 7,7,8,8-tetracyanoquinodimethane and *p*-benzoquinone (~0.83 eV).

0022-3263/84/1949-5002$01.50/0