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Registry No. 1-Adamantanol, 768-95-6; 2-norborneol, 1632-68-4; *tert*-butanol, 75-65-0; 1-methylcyclopentanol, 1462-03-9; 1-methylcyclohexanol, 590-67-0; 2-methyl-2-butanol, 75-85-4; 3-methyl-3-pentanol, 77-74-7; 2-methyl-2-norborneol, 5240-73-3; *tert*-cumyl alcohol, 617-94-7; *p*-CH₃-*tert*-cumyl alcohol, 1197-01-9; benzhydrol, 91-01-0; trityl alcohol, 76-84-6.

Liquid-Crystalline Cation-Radical Charge-Transfer Systems

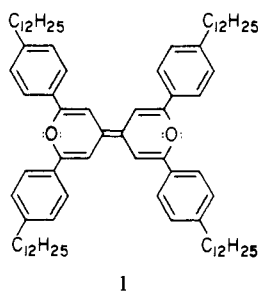
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The effect of molecular ordering on physicochemical properties is receiving increased attention. Of special interest is the study of anisotropic chemical,¹ electrical,² magnetic,³ and optical⁴ properties of ordered molecular species in the solid state. Electronic conductivity, for example, in certain organic and inorganic crystals requires the formation of segregated columns of an electron donor, e.g., tetrathiofulvalene (TTF), and an electron acceptor, e.g., 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), in a single crystal.² The redox behavior of the aligned molecular species and the degree of charge transfer are also important in determining electronic conductivity.⁵

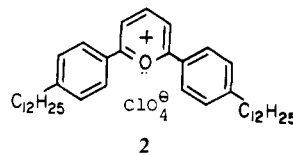
We have attempted to control molecular stacking of one of the charge-transfer partners by introducing hydrophobic interactions in an electron-donor molecule capable of forming a stable cation radical. We report the first synthesis of discotic liquid-crystalline cation-radical charge-transfer salts of a $\Delta^{4,4}$ -bi-4*H*-pyran derivative (**1**) and describe their mesomorphic behavior as a function of the



1

counterion. Some charge-transfer properties of the salts will also be described.

The neutral 2,2',6,6'-tetraphenylbipyran-4-ylidene derivative **1** was synthesized in 71% yield from the pyrylium salt **2** and tributylphosphine.⁶ The physical properties of **1** agreed with those



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previously reported.⁷ Compound **1** has a discotic mesophase between 90 and 149 °C.⁷ The discotic-to-isotropic thermal transition in **1** has a larger enthalpy (6.4 kcal/mol) than the crystal-to-discotic and the crystal-to-crystal thermal transitions. This is characteristic of the highly ordered discotic mesophase.⁷ Compound **2** also shows mesomorphic behavior. The pyrylium salt **2** showed smectic mesomorphism between 117 and 139.5 °C.

The formation of a column of disk-shaped molecules is characteristic of discotic mesophases.⁸ In a discotic mesophase the molecular species align to provide the most effective interaction of the hydrocarbon chains. This type of phase is desirable for strong interchromophore interactions⁸ and is the basis for the effects we hope to achieve.

The oxidation potentials for **1**, determined by cyclic voltammetry, are $E_1^\circ = +0.17$ V and $E_2^\circ = +0.56$ V [vs. a saturated calomel electrode (SCE) in methylene chloride solution].⁹ Cation radicals **1a** ($1^+ \cdot \text{BF}_4^-$) and **1b** ($1^+ \cdot \text{ClO}_4^-$) were synthesized electrochemically by constant-potential electrolysis.⁹ The corresponding TCNQ salt (**1c**) was synthesized by mixing equal molar concentrations of **1** and TCNQ in ethyl acetate at room temperature. The TCNQ charge-transfer salt crystallized from solution as an analytically pure 1:1 complex. All of the cation radicals gave excellent combustion analyses, and their electronic spectral behavior was consistent with that of their dealkylated derivatives.¹⁰ Compounds **1a-c** show discotic mesomorphic behavior over a broad temperature range >90 °C. The extended mesomorphic range of the cation-radical salts suggests that intermolecular interactions in the cation-radical salts are effective at providing stable discotic liquid crystalline phases.

The thermal transitions and mesophases (Table I) were characterized by a combination of optical microscopy and differential scanning calorimetry (DSC). The degree of supercooling of discotic-to-discotic and crystal-to-discotic transitions is characteristically less than for the crystal-to-crystal thermal transitions.¹¹

The TCNQ salt (**1c**) is unique among the three charge-transfer salts in that it has very low fluidity in the mesomorphic phase. The mesomorphic phase of **1c** resembles the crystalline phase more closely than does that of **1** or even **1a** and **1b**. In general, the salts **1a-c**, which are stable in the crystalline and mesomorphic phases, chemically decompose at a temperature that seems to correspond to the mesomorphic-to-isotropic thermal transition at ~240–262 °C.

Intense charge-transfer absorption is observed for the cation radicals in solution (1030 nm in CH₂Cl₂) and in the solid state (1450 nm for crystalline particles in an ethyl cellulose polymer film),⁴ which suggests a structure with strong intermolecular interactions. There seems to be a direct correlation between mesophase range and the type and degree of intermolecular interaction. In the neutral species **1**, hydrophobic interactions are essential for mesophase formation. The tetrafluoroborate **1a** and

(6) Reynolds, G. A.; Chen, C. H. *J. Heterocycl. Chem.* **1981**, *18*, 1235.

(7) Fugnitto, R.; Strzelecka, H.; Zann, A.; Dubois, J. C. *J. Chem. Soc., Chem. Commun.* **1980**, 271–272.

(8) Vauchier, C.; Zann, A.; LeBarry, P.; Dubois, J. C.; Billard, J., *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 103–114.

(9) A Princeton Applied Research Model 173 potentiostat and a Model 175 universal programmer were used in the standard three-electrode configuration to obtain the oxidation potentials of **1** by cyclic voltammetry. A platinum inlay electrode was used as the working electrode along with a platinum auxiliary electrode and a fiber standard calomel electrode. The electrolyte was 0.1 M tetrabutylammonium fluoroborate for the synthesis of **1a** and tetraethylammonium perchlorate for the synthesis of **1b** in methylene chloride.

(10) Deuchert, K.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 875–886.

(11) Bouligand, Y. *J. Phys. (Paris)* **1980**, *44*, 1307–1315.

(1) Kress, R. B.; Duesler, E. N.; Etter, M. C.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1980**, *102*, 7709–7714.

(2) Epstein, A. J.; Miller, J. S. *Sci. Am.* **1979**, *241*, 52–61.

(3) Goodenough, J. B. In "Magnetism"; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1963; Vol. 3, pp 1–62.

(4) Saeva, F. D.; Olin, G. R.; Ziolo, R. F.; Day, P. *J. Am. Chem. Soc.* **1979**, *101*, 5419–5421.

(5) Bloch, A. N.; Carruthers, T. F.; Poehler, T. O.; Cowan, D. O. "Chemistry and Physics of One-Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: New York, 1977; pp 47–84.

Table I. Thermal Transitions for Mesomorphic Compounds 1, 1a-1c, and 2

compd	temp, °C	$\Delta H,^a$ cal/mol	$\Delta S,^a$ cal/ (mol K)	transition ^{a,b}
1	34.5	3690	12.0	K ₁ → K ₂
	41	421	1.3	K ₂ → K ₃
	46	189	0.6	K ₃ → K ₄
	90	1780	4.9	K ₄ → D ₁
	149	6390	15.2	D ₁ → I
1a	95	4180	11.3	K ₁ → K ₂
	142.5	4340	10.4	K ₂ → D ₁
	155	5090	11.9	D ₁ → D ₂
	~240 dec			D ₂ → I
1b	106.5	4200	11.1	K ₁ → K ₂
	144.5	3820	9.1	K ₂ → D ₁
	157	4690	10.9	D ₁ → D ₂
	261.5 dec			D ₂ → I
1c	11	3710	13.1	K ₁ → D ₁
	34	2860	9.3	D ₁ → D ₂
	242.5 dec			D ₂ → I
2	117	4170	10.7	K → S ₁
	137	1090	2.7	S ₁ → S ₂
	139.5	1330	3.2	S ₂ → I

^a Differential scanning calorimetry. ^b From optical microscopy: K = crystal; S = smectic mesophase; D = discotic mesophase; I = isotropic.

Table II. Type of Attractive Interaction vs. Mesophase Range

compd	mesophase range, °C	type of attractive interaction
1	59	hydrophobic
1a	97.5	hydrophobic, cation-radical CT
1b	117	hydrophobic, cation-radical CT
1c	231.5	hydrophobic, cation-radical CT and anion-radical CT

perchlorate **1b** cation-radical salts, on the other hand, show hydrophobic as well as cation-radical/cation-radical charge-transfer (CT) interactions. The TCNQ salt **1c** can show anion-radical/anion-radical CT¹² in addition to hydrophobic and cation-radical/cation-transfer interactions (see Table II).

The cation-radical species also form charge-transfer complexes with **1** in solution. This CT band occurs at 830 nm in CH₂Cl₂, which corresponds to an activation energy (E_a) for self-exchange, i.e., electron transfer between **1** and **1a**, of ~9.2 kcal/mol, with the relationship $E_a = \Delta E_{CT}/4$.¹³

The electronic conductivity of the TCNQ salt **1c** is $<10^{-6} \Omega^{-1} \text{cm}^{-1}$.¹⁴ This low conductivity is attributed to the fact that there is complete charge transfer between **1** and TCNQ, as shown by the nitrile stretching frequency¹⁵ (2179 cm⁻¹) in the infrared, and not to the lack of a segregated stacked structure.

In summary, tetraphenyl- $\Delta^{4,4}$ -bi-4H-pyran cation radicals with four dodecyl groups have a discotic mesophase over the range 97–230 °C, depending on the counterion. In general, the cation radicals have a mesomorphic range that is considerably larger than that of the neutral species, presumably because of enhanced intermolecular interactions of the charge-transfer type. The observed charge-transfer absorption further suggests the formation of columns of disk-shaped molecules. We suggest that the tendency to form mesomorphic structures may provide valuable information for design of molecular crystals with a predictable structure.

Registry No. **1**, 75817-94-6; **1a**, 81740-35-4; **1b**, 81740-36-5; **1c**, 81740-37-6; **2**, 75818-00-7.

(12) Bozio, R.; Zanon, A.; Giraldo, A.; Pecile, C. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 235-248.

(13) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966-978.

(14) Perlstein, J., private communication.

(15) Chappell, J. S.; Block, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442-2443.

Anion Receptor Molecules. Chain Length Dependent Selective Binding of Organic and Biological Dicarboxylate Anions by Ditopic Polyammonium Macrocycles[†]

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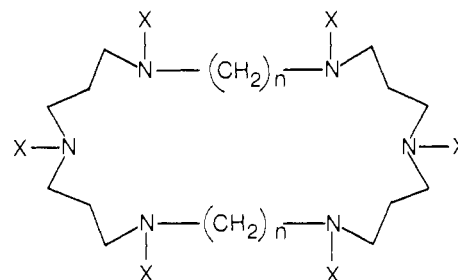
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Anion binding by organic ligands has made significant progress in recent years. Macrocyclic and macropolycyclic polyammonium molecules have been shown to complex strongly and selectively a variety of inorganic and organic anions, thus laying the basis for developing a field of anion coordination chemistry.^{1,2} The anion complexation unit of these receptor molecules consists of several positively charged binding sites arranged symmetrically around a cavity defined by the molecular architecture.

Macropolycyclic coreceptors that contain two or more binding subunits may complex two or more substrates, forming di- or polynuclear cryptates;³ on the other hand, the subunits may cooperate for the multiple binding of a polyfunctional substrate. Thus, cylindrical macropolycyclics form selective cryptates of diammonium ⁺H₃N-(CH₂)_m-NH₃⁺ cations, bound by each terminal NH₃⁺ group, with a stability and a selectivity depending on the complementarity between the length of the substrate and the cavity size of the receptor.^{4,5}

We have now incorporated such polyfunctional substrate binding features in the design of ditopic coreceptor molecules for dianionic substrates. We report here the synthesis of two new hexaaza-macrocycles, **1** and **2**, as well as preliminary studies of the re-



- 1, $n = 7$; X = H
2, $n = 10$; X = H
3, $n = 3$; X = H
16, $n = 7$; X = Ts
17, $n = 10$; X = Ts

markable complexation properties of their fully protonated forms **1-6H⁺** and **2-6H⁺** toward dicarboxylate substrates ⁻O₂C-R-CO₂⁻.

The synthesis of **1** and **2** follows a reaction sequence similar to that used earlier for the related macrocycle **3**.¹ Tosylation of 1,7-diaminoheptane yields **4** (mp 144 °C, 97% yield), which is

[†] ERA No. 265 of the CNRS.

(1) Dietrich, B.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1282-1283 and references therein.

(2) Kimura, E.; Sakonaka, A.; Yatsunami, T.; Kodama, M. *J. Am. Chem. Soc.* **1981**, *103*, 3041-3045. Peter, F.; Gross, M.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *J. Chem. Soc., Chem. Commun.* **1981**, 1067-1069. Margulis, T. N.; Zompa, L. J. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1426-1428. Wester, N.; Vögtle, F. *Chem. Ber.* **1980**, *113*, 1487-1493.

(3) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49-57; *Pure Appl. Chem.* **1980**, *52*, 2441-2459; In "IUPAC Frontiers of Chemistry"; Laidler, K. J., Ed.; Pergamon Press: Oxford and New York, 1982; pp 265-272.

(4) Johnson, M. R.; Sutherland, I. O.; Newton, R. F. *J. Chem. Soc., Chem. Commun.* **1979**, 309-311. Mageswaran, R.; Mageswaran, S.; Sutherland, I. O. *Ibid.* **1979**, 722-724. Jones, N. F.; Kumar, A.; Sutherland, I. O. *Ibid.* **1981**, 990-992.

(5) Kotzyba-Hibert, F.; Lehn, J. M.; Vierling, P. *Tetrahedron Lett.* **1980**, 941-944; Kotzyba-Hibert, F.; Lehn, J. M.; Saigo, K. *J. Am. Chem. Soc.* **1981**, *103*, 4266-4268. Kintzinger, J. P.; Kotzyba-Hibert, F.; Lehn, J. M.; Pagelot, A.; Saigo, K. *J. Chem. Soc., Chem. Commun.* **1981**, 833-836.