with 0.4 mL of 1 M boron tribromide in *n*-hexane under argon at 70 °C. After 2.5 h the TLC spot (chloroform) for the previously not isolated product reached its maximum size, and 6 mL of cold water was added to the reaction mixture with stirring. The resulting mixture was extracted with ether. Removal of the ether gave 70 mg of gray solid, which was chromatographed, eluting with chloroform, to give 55 mg (59% yield) of yellow crystals, which was recrystallized from hexane to give product: mp 106–106.5 °C; $^1$H NMR ($CDCl_3$, 60 MHz) $\delta$ 3.84 (s, 3 H, $CH_3$), 5.01 (s, 1 H, OH), 6.11–6.69 (m, 6 H, Ar H).

Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.79; H, 5.09. Found: C, 79.16; H, 5.44.

**Determination of Ionization Constants.** Buffer solutions were prepared by the method of Kolthoff,[15] with borate buffers being used for the pH range up to 10 and carbonate buffers for the pH range 10–11. Sodium hydroxide solutions were used for higher pHs. In a specific case, 100 $\mu$L of 0.003811 M 1-biphenylenol solution was syringed into 25 mL of each of 17 buffer solutions. The UV spectrum of each of the resulting solutions was measured over the range 300–240 nm at 26 °C.

**Registry No.** 1,8-Bisphenylenediol, 18798-64-6; 2,7-dimethyl-1,8-biphenylenediol, 98991-01-6; 1,5-biphenylenediol, 98991-02-7; 1-biphenylenol, 1078-07-5; 8-methoxy-1-biphenylenol, 98945-48-3; 2-methyl-5-nitrophenol, 5428-54-6; 2-iodo-6-methyl-3-nitrophenol, 98991-03-8; 2-iodo-6-methylanisole, 25922-05-8; 2,2′-dimethoxy-3,3′-dimethyl-6,6′-dinitrobiphenyl, 98991-04-9; 2,2′-dimethoxy-3,3′-dimethyl-6,6′-diaminobiphenyl, 98991-05-0; 2,2′-dimethoxy-3,3′-dimethyl-6,6′-diiodobiphenyl, 98991-06-1; 1,8-dimethoxy-2,7-dimethylbiphenylene, 98991-07-2; 2-iodo-3-nitroanisole, 98991-08-3; 2-iodo-3-aminoanisole, 98991-09-4; 2,3-diiodoanisole, 98991-10-7; 1,5-dimethoxybiphenylene, 98991-11-8; 1,8-dimethoxybiphenylene, 18798-67-9.

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# Double-Hydrogen-Bonding Catalysis of the Reaction of Phenyl Glycidyl Ether with Diethylamine by 1,8-Biphenylenediol[1]

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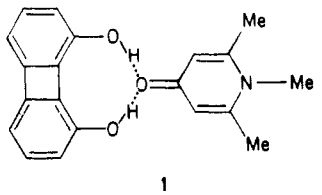
The reaction of phenyl glycidyl ether with diethylamine in butanone gives 3-(diethylamino)-1-phenoxy-2-propanol. Catalysis by phenol and five of its meta- and para-substituted derivatives gives catalysis constants that obey the Brønsted equation well, with an $\alpha$ value of 0.18. The catalysis constants for 1-biphenylenol and 8-methoxy-1-biphenylenol are in good agreement with the Brønsted equation, as is the value for catechol, when the rate constant and acidity constant have been divided by two. The catalysis constant for 1,8-biphenylenediol is about six times as large and hence the value per hydroxy group is about three times as large as calculated from the Brønsted equation. The 1,8-diol, whose adducts with several oxygen bases are known from X-ray crystal structure determinations to have two hydrogen bonds from the hydroxy groups of the diol to the same oxygen atom of the base, is apparently giving double-hydrogen-bonding catalysis. This double-hydrogen-bonding catalysis gives 1,8-biphenylenediol a catalytic activity, per hydroxy group, of a phenol that is 600 times as strong an acid.

1,8-Biphenylenediol has been found to form crystalline complexes with 1,2,6-trimethyl-4-pyridone (1), *N,N,N′,N′,N″,N″*-hexamethylphosphoramide, and 2,6-dimethyl-$\gamma$-pyrone in which there are two strong hydrogen bonds from one molecule of the diol to the same oxygen atom of the base.[2] In addition, the 1,8-diol gives equilibrium

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constants for hydrogen bonding to several oxygen bases in cyclohexane that are larger, by as much as 50-fold, than those for hydrogen bonding of the same bases to *m*-nitrophenol, whose ionization constant per hydroxy group in water is about the same as that of the 1,8-diol.[3] This evidence of the ability of the 1,8-diol to form two hydrogen bonds to the same oxygen atom made us wonder about its ability to act as an acidic catalyst, especially in a reaction where the acid catalyst acts by hydrogen bonding.

Partansky has studied the reaction of phenyl glycidyl ether with diethylamine[4] at 25 °C in butanone by measuring the extent of reaction after 24 h and after 48 h. He found that the reaction was catalyzed by hydroxy compounds with a crude correlation between catalytic ability and the acidity of the catalyst. Relative catalytic activities were found, for example, to be salicylic acid > *m*-nitrophenol, *p*-chlorophenol > phenol > benzoic acid > methanol. However, the 4% of reaction that occurred after 24 h in the absence of catalyst was increased only to 11.4% by 0.2 M methanol and 33.5% by 0.05 M salicylic acid. The fact that the changes in catalytic activity tend to be so much smaller than the changes in catalyst acidity suggested that there was not a large amount of proton transfer from the catalyst in the transition state of the rate-controlling step. However, the situation must be complicated by hydrogen bonding of the catalyst to the solvent and the amine as well as to the epoxide.

The reaction had already been reported to give 1-(diethylamino)-3-phenoxy-2-propanol[5] (eq 1), on the basis of elemental analysis of the hydrochloride[6] and of analogy

(1) (a) This investigation was supported in part by NSF Grant CHE-8114770. (b) A preliminary report of the present results was given in: Hine, J.; Linden, S.-M.; Kanagasabapathy, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 1082–1083.

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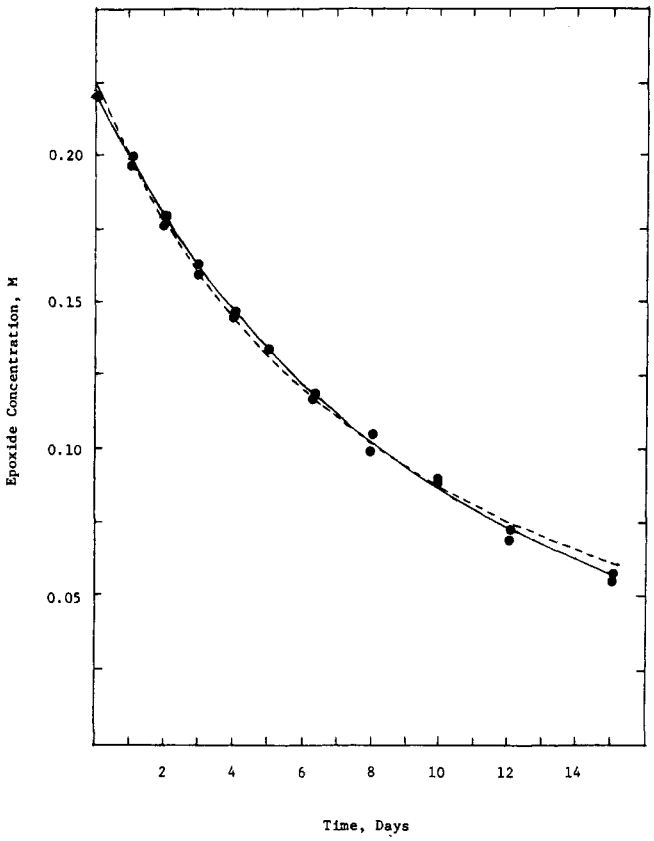


**Figure 1.** Plot of concentration of phenyl glycidyl ether vs. time for a run with no added catalyst. The dashed line is the theoretical line if autocatalysis is neglected. The solid line allows for autocatalysis.

to the earlier reported reaction of ammonia with *o*-tolyl glycyl ether.[7]

$$PhOCH_2\overline{CHCH_2O} + Et_2NH \rightarrow PhOCH_2CH(OH)CH_2NEt_2 \quad (1)$$

Evidence that carcinogenic polynuclear aromatic hydrocarbons are transformed to epoxides in living organisms and that these epoxides then attack nucleic acids[8-10] provides an additional reason for the present study.

## Results

The kinetics of the reaction of phenyl glycidyl ether with diethylamine in butanone was followed by GLC measurements in which the height of the ether peak was compared with that of a peak due to naphthalene, which was present (~0.08 M) as a reference compound. A plot of ether concentration against time is shown in Figure 1 for a run using 0.2213 M initial ether, 0.3432 M initial amine, and no added catalyst. The dashed line in the figure was calculated from the assumption that the reaction is a simple second-order process kinetically. The tendency of the later experimental points to lie above this line is not a very large one, but it suggests that the reaction is catalyzed appreciably by the product, an alcohol. It was therefore assumed that the reaction was autocatalyzed and

**Table I. Catalysis Constants for Reaction of Diethylamine with Phenyl Glycidyl Ether[a]**

| catalyst | $10^5 k_c$, $M^{-2}$ $s^{-1}$ | $pK_a$[b] |
|---|---|---|
| phenol | 6.0 | 9.99 |
| *p*-chlorophenol | 7.7 | 9.41 |
| *m*-chlorophenol | 8.2 | 9.12 |
| *m*-nitrophenol | 14.3 | 8.36 |
| *p*-cyanophenol | 15.3 | 7.97 |
| *p*-nitrophenol | 17.0 | 7.15 |
| catechol | 11.9 | 9.36 |
| 1-biphenylenol | 11.5 | 8.64[c] |
| 8-methoxy-1-biphenylenol | 7.3 | 9.15[c] |
| 1,8-biphenylenediol | 75 | 8.01[c] |

[a] In butanone solution at 30 °C. Calculated using eq 3. [b] In water at 25 °C. Obtained, unless otherwise noted, from: Serjeant, E. P.; Dempsey, B. "Ionization Constants of Organic Acids in Aqueous Solution"; Pergamon Press: New York, 1979. [c] Hine, J.; Hahn, S.; Miles, D. E.; Ahn, K. *J. Org. Chem.*, preceding paper in this issue.

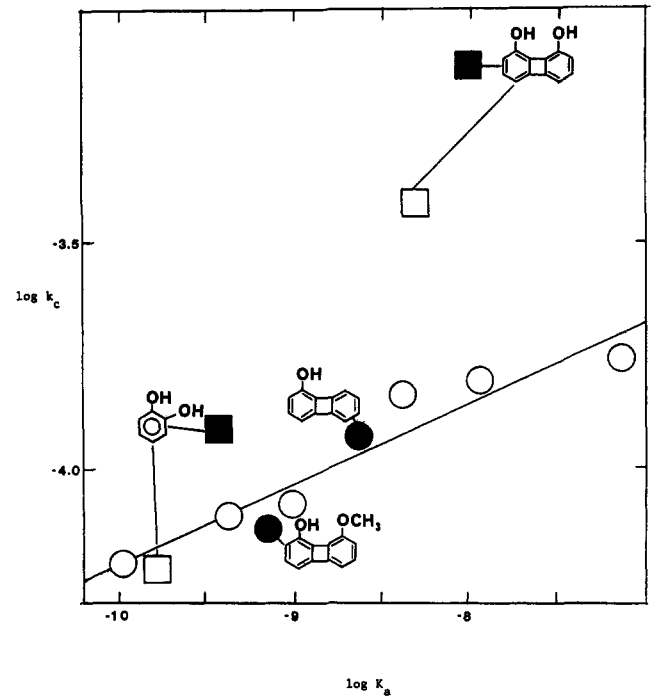


**Figure 2.** log–log plot of catalysis constants in the reaction of diethylamine with phenyl glycidyl ether vs. ionization constants for the catalyst. (○) Meta- and para-substituted phenols, (●) monohydroxy derivative of biphenylene, (■) uncorrected data for a diol, (□) statistically corrected data for a diol.

obeyed eq 2, in which E is the ether, N is the amine, and A is the alcohol product. The nonlinear least-squares best

$$-d[E]/dt = (k_u + k_a[A])[E][N] \quad (2)$$

values of $k_u$ and $k_a$ gave the solid line shown in Figure 1. Improvement in the fit of the calculated to the experimental ratios of peak heights was produced by the assumption of autocatalysis in all the runs that were made without added catalyst. The calculated values of $k_u$ varied by ±7% and the values of $k_a$ by ±44% in different runs but high values of $k_u$ were obtained with low values of $k_a$. The value of $k_u + k_a$ [A] that could be calculated at half reaction varied less than ±8%. The best values are $3.5 \times 10^{-6}$ $M^{-1}$ $s^{-1}$ for $k_u$ and $9.4 \times 10^{-6}$ $M^{-2}$ $s^{-1}$ for $k_a$.

In the presence of a phenol the kinetics were assumed to obey eq 3. Values of $k_c$ were calculated using the values of $k_u$ and $k_a$ obtained without added catalyst. Decreasing

$$-d[E]/dt = (k_c[ArOH] + k_u + k_a[A])[E][N] \quad (3)$$

$k_u$ by 7% while increasing $k_a$ by 44% changed $k_c$ by less

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than 1%. The phenol concentrations were in the range 0.0578–0.1485 M except for 1,8-biphenylenediol, for which the concentration range was 0.0297–0.0411 M. Variations in the initial catalyst concentration, 2.5-fold for *p*-nitrophenol but less for other catalysts, were not accompanied by any clear trend in the values of $k_c$ obtained. The fraction of the total reaction that is background reaction, $f_B$, is defined in eq 4, in which A is the concentration of product formed at half reaction. In the runs with added

$$f_B = (k_a + k_u[A])/(k_c[ArOH] + k_u + k_a[A]) \quad (4)$$

catalysts $f_B$ ranged from 0.13 to 0.40. The average value of $k_c$ obtained from at least two kinetic runs is listed for each catalyst in Table I, along with p$K_a$ values in aqueous solution at 25 °C. The Brønsted plot in Figure 2 shows that phenol and its meta- and para-substituted derivatives give satisfactory agreement with the Brønsted equation. The Brønsted $\alpha$ is 0.18. The agreement of the points for 1-biphenylenol, 8-methoxy-1-biphenylenol, and, after statistical correction, catechol with the Brønsted line is approximately as good as that of the meta- and para-substituted phenols.

Even after statistical correction the $k_c$ value for 1,8-biphenylenol is about three times as large as would be expected from the Brønsted correlation. In the case where a reaction rate is as slightly sensitive to the acidity of the catalyst as the present case, this corresponds to a marked difference in effective acidities. According to the Brønsted plot it would take a monohydroxylic phenol that is 600 times as acidic to have the same catalytic activity, per hydroxy group, as the 1,8-diol.

It should be remembered that we are comparing reaction rates in butanone with p$K_a$ values in water. If the 1,8-diol were much more acidic in butanone than would be expected from its acidity in water, the point for the 1,8-diol in Figure 2 could fall on the line if the plot of log $k_c$ were vs. log $K_a$ values determined in butanone. However, we can think of no plausible reason why the acidity in butanone should be so large. The monoanion of the 1,8-diol cannot be stabilized by internal hydrogen bonding because the oxygen atoms are much too far apart.[2]

The fact that the opening of the epoxide ring is acid catalyzed shows that the oxygen atom has become more basic in the transition state of the uncatalyzed reaction than it was in the reactant.[11] It does not show whether this oxygen atom has become more basic in the transition state of the acid-catalyzed reaction. The observation of especially efficient catalysis by 1,8-biphenylenediol suggests that the first hydrogen bond formed by a phenol is not strong enough to have made this oxygen less basic in the transition state; therefore, formation of a second hydrogen bond occurs and leads to added stability.

We found the product isolated from several reactions, including one with catalysis by the 1,8-diol, to be the same. Its 500-MHz $^1$H NMR spectrum and $^{13}$C NMR spectrum are consistent with the structure, 1-(diethylamino)-3-phenoxy-2-propanol, that had been assigned by earlier workers.[4-6] For example, the $^{13}$C chemical shift of the hydroxylated carbon atom (the only aliphatic carbon that gives a doublet in off-resonance decoupling) is 66.03 ppm, which is 10 ppm higher than that of any other carbon except the phenoxylated carbon. According to empirical correlations of $^{13}$C chemical shifts,[12] none of the other structural features of the molecule should be nearly capable of reversing the larger chemical shifts put on the two carbon atoms that have oxygen attached directly to them.

## Experimental Section

**Chemicals.** The 1,8-biphenylenediol,[13,14] 1-biphenylenol,[15] and 8-methoxy-1-biphenylenol[16] used were prepared by modifications of known procedures. The solvent, reactants, and other catalysts that were used were high quality commercially available chemicals that were purified further before use.

**Kinetic Runs.** Measured volumes of stock solutions of phenyl glycidyl ether and naphthalene, diethylamine, and catalyst, each in butanone, were syringed into a 5-mL round-bottomed flask, giving about 2 mL of a solution that was ordinarily about 0.2 M in ether, 0.08 M in naphthalene, and 0.3 M in amine. The solution was promptly mixed and about 70 μL samples added to each of about 30 capillary tubes (~1.6 × 90 mm), which were then cooled in a dry ice bath. The capillary tubes were then sealed, two were analyzed by GLC on an F & M Model 720 instrument using a 6-ft $^1/_4$-in. column packed with 10% UCON 50-HB2000 on 80/100 Supelcoport at 160 °C, and the remainder were placed in a water bath kept at 30 ± 0.1 °C. About 1 min passed between the time the reactants were mixed and the time the first capillary tube was cooled and about 9 min more passed before the last tube was cooled. The amount of reaction taking place during this time at room temperature (about 24 °C) was neglected. The fastest reaction had a half-time of about 24 h. In the GLC analysis the diethylamine and butanone were eluted almost immediately and other retention times were as follows: naphthalene, 3 min; phenyl glycidyl ether, 7.5 min; phenol, 5.5 min; *p*-chlorophenol, 26 min; *m*-chlorophenol, 27 min; 1-(diethylamino)-3-phenoxy-2-propanol, 38 min. No peaks for the cyanophenol, nitrophenols, or biphenylenols were observed.

Measurements on solutions containing only the ether and naphthalene showed that the ratio of the ether concentration to the naphthalene concentration divided by the ratio of the GLC peak height for the ether to the GLC peak height for naphthalene should be about 2.2. A few early kinetic runs, for which this quotient for the zero point differed markedly from 2.2 for unknown reasons, were discarded. All the runs that were used had a quotient of 2.21 ± 0.08, except for the runs with catechol, where it was 2.08.

**Reaction Product.** A sample of 100 mL of 0.231 M phenyl glycidyl ether, 0.376 M diethylamine, and 0.132 M *p*-nitrophenol in butanone was kept at 35 °C for 15 days. Vacuum distillation gave 4.434 g (86% yield) of very light yellow viscous liquid: bp 127 °C (1 mm); $^1$H NMR ($CDCl_3$, 500 MHz) δ 1.03 (t, $J$ = 7.1 Hz, 6, $CH_3$), 2.52–2.64 (m, 6, $CH_2N$), 3.80 (br s, 1, OH), 3.95–4.05 (m, 3, $OCH_2CH$), 6.90–6.95 (m, 3, ortho and para H), 7.24–7.27 (m, 2, meta H); $^{13}$C NMR ($CDCl_3$, 500 MHz, multiplets listed are those obtained in the off-resonance mode) δ 11.99 (q, $CH_3$), 47.26 (t, $CH_3CH_2$), 56.02 (t, $CH_2NEt_2$), 66.03 (d, CHOH), 70.49 (t, $CH_2O$), 77.12 (t, $CDCl_3$), 114.95 (d, meta C), 120.86 (d, para C), 129.41 (d, ortho C), 158.89 (s, $C_{Ar}O$). Product with the same $^1$H NMR spectrum was obtained in 90% yield from 5 mL of butanone that was 0.205 M in phenyl glycidyl

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ether, 0.302 M in diethylamine, and 0.0312 M in 1,8-biphenylenediol.

**Registry No.** Diethylamine, 109-89-7; phenylglycidyl ether, 122-60-1; phenol, 108-95-2; *p*-chlorophenol, 106-48-9; *m*-chlorophenol, 108-43-0; *m*-nitrophenol, 554-84-7; *p*-cyanophenol, 767-00-0; *p*-nitrophenol, 100-02-7; catechol, 120-80-9; 1-biphenylenol, 1078-07-5; 8-methoxy-1-biphenylenol, 98945-48-3; 1,8-biphenylenediol, 18798-64-6; 1-(diethylamino)-3-phenoxy-2-propanol, 15288-08-1.

# Kinetics of the Reaction of Alkylamines with 7,7,8,8-Tetracyanoquinodimethane (TCNQ) in Organic Solvents

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The following sequence of substitution reactions was studied spectrophotometrically in organic solvents:

$$RNH_2 + TCNQ \xrightarrow{-HCN} \text{7-substituted TCNQ} \underset{-HCN}{\overset{+RNH_2}{\rightleftharpoons}} \text{7,7-disubstituted TCNQ}$$

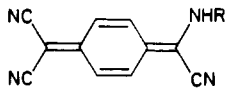
where R = butyl, octyl, dodecyl, and hexadecyl. The production of 7-(alkylamino)-7,7,8-tricyanoquinodimethanes proceeds via the formation of the anion radical of TCNQ ($TCNQ^{-}\cdot$) whose rate of appearance was found to be a function of the chain length of R, reaching a maximum for octylamine. The formation of $TCNQ^{-}\cdot$ was sensitive to the solvent polarity and electron-donor power and was associated with a small enthalpy and a highly negative entropy of activation. Above a certain $[C_8H_{17}NH_2]$ the rate of disappearance of $TCNQ^{-}\cdot$ was independent of the amine concentration, and the reaction had a much higher enthalpy and entropy of activation. The occurrence of tautomerism precluded an investigation of the conversion of 7-(octylamino)-7,8,8-tricyanoquinodimethane into 7,7-bis(octylamino)-8,8-dicyanoquinodimethane. A study of the reaction of octylamine with 7-morpholino-7,8,8-tricyanoquinodimethane (which does not exist in tautomeric forms) showed that the second substitution step proceeds with the same mechanism as the first one. The only difference between the two compounds (TCNQ and its monosubstituted morpholino derivative) is one of reactivity.

The strong Lewis acid 7,7,8,8-tetracyanoquinodimethane (TCNQ) forms a myriad of charge-transfer complexes and salts with very interesting properties[2-5] and undergoes substitution reactions[2,3,6] similar to nucleophilic vinylic substitutions.[7] Little attention has been given, however, to studying the kinetics and mechanism of formation of TCNQ derivatives.[3,8] The use of this dye to determine the critical micelle concentration of surfactants[10] is complicated due to the occurrence of side reactions, especially with alkylammonium carboxylates.[11] As a first step in investigating this micelle-mediated interaction we studied the kinetics of the reaction of alkylamines with TCNQ in organic solvents. Our results showed that the reaction rate was dependent on the amine structure and the solvent used.

## Experimental Section

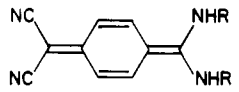
Melting points were not corrected. The spectrometers used were Zeiss DMR-21, PM6KS (UV–vis), Perkin-Elmer 238 (IR), Varian T-60, EM-360 ($^1$H NMR). The solvents, alkylamines, and TCNQ (Aldrich and Merck) were purified as given elsewhere.[12,13]

The reaction between TCNQ and an amine, e.g., $RNH_2$, can produce mono- (type I) and/or disubstituted derivative (type II) as depicted. The preparation of these derivatives for compounds with R = butyl, octyl, and dodecyl was given elsewhere,[11] those for R = hexadecyl were similarly prepared. The following results were obtained: the purple brown 7-(hexadecylamino)-7,8,8-tricyanoquinodimethane had a mp of 98–99 °C. Anal. Calcd for $C_{27}H_{38}N_4$: C, 77.47; H, 9.15; N, 13.38. Found: C, 77.41; H, 9.15; N, 13.48. IR (KBr) $\nu_{N-H}$ 3225, $\nu_{C-H}$ 3030, $\nu_{C\equiv N}$ 2201, 2188, and $\nu_{C=C}$ 1610 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.88 (t, 3 H), 1.34 (s, 28 H), 1.85 (m, 2 H), 4.00 (t, 1 H), 7.88 (q, 4 H). The yellow 7,7-bis(hexadecylamino)-8,8-dicyanoquinodimethane had a mp of 219–221 °C. Anal. Calcd for $C_{42}H_{72}N_4$: C, 79.68; H, 11.46; N, 8.85. Found: C, 79.52; H, 11.34; N, 8.74. IR (KBr) $\nu_{N-H}$ 3192, 3104, $\nu_{C-H}$ 3050, $\nu_{C\equiv N}$ 2181, 2138, and $\nu_{C=C}$ 1600 $cm^{-1}$; $^1$H NMR




type I compound

7-(alkylamino)-7,7,8-tricyanoquinodimethane




type II compound

7,7-bis(alkylamino)-8,8-dicyanoquinodimethane

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(1) (a) Divisão, Têcnica, Hoechst do Brasil, Suzano, S.P. (b) UNESP, Botucatu, S.P.

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