613-90-1; **11,** 56630-25-2; thionyl chloride, 7719-09-7; methanol, 67-56-1.

References and Notes

(1) S. Yanagida and S. Komori, *Synthesis,* 189 (1973).
(2) L. J. Bellamy, "Advances in Infrared Group Frequencies", Methuen, London, 1968, p 197.
(3) R. M. Moriarty, *J. Org. Chem.,* **30,** 600 (1965).
(4) I. B. Douglass, *J. Org. Chem.,* **30,** 633 (1965).
(5) R. V. Norton and I. B. Douglass, *Org. Magn. Reson.,* **6,** 89 (1974).
(6) The recovery of **1c** was 85% (determined by GLC analysis of the volatile material).
(7) L. I. Peterson, *J. Am. Chem. Soc.,* **89,** 2677 (1967).
(8) S. Yanagida, T. Fujita, M. Ohoka, I. Katagiri, and S. Komori, *Bull. Chem. Soc. Jpn.,* **46,** 292 (1973).
(9) W. A. Sheppard and J. Diekmann, *J. Am. Chem, Soc.,* **86,** 1891 (1964).
(10) J. F. King and T. Durst, *Can. J. Chem.,* **44,** 819 (1966).
(11) A. M. Hamid and S. Trippett, *J. Chem. Soc. C,* 1612 (1968).
(12) B. Zwanenburg and J. Strating, *Q. Rep. Sulfur Chem.,* **5,** 79 (1970).
(13) G. Simchen and W. Krämer, *Chem. Ber.,* **102,** 3656 (1969).
(14) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, p 372.
(15) A. J. Krubsack and T. Higa, *Tetrahedron Lett.,* 5149 (1968).
(16) A. J. Krubsack, T. Higa, and W. E. Slack, *J. Am. Chem. Soc.,* **92,** 5258 (1970).
(17) J. Strating, L. Thijs, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas,* **86,** 641 (1967).
(18) Melting points were determined on a Yanagimoto micro melting point apparatus. Melting points and boiling points were uncorrected. Ir spectra were recorded on Japan Electroscopic IR-E (4000–600 cm^{-1}) and EPI-L (700–200 cm^{-1}) spectrophotometers. NMR spectra were obtained on a Japan Electron Optics JNM-G-60 spectrometer with tetramethylsilane as an internal reference. Mass spectra were obtained on a Hitachi RMU-6E spectrometer.
(19) L. M. Yagupol'skii and R. V. Belinskaya, *Zh. Obshch. Khim.,* **28,** 772 (1958); *Chem. Abstr.,* **52,** 17167 (1958).
(20) T. S. Oakwood and C. A. Weisgerber, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 112.
(21) D. G. Coe, M. M. Gale, R. P. Linstead, and C. J. Timmons, *J. Chem. Soc.,* 123 (1957).
(22) The spectrum was recorded on a Hitachi 225 spectrophotometer equipped with gratings.
(23) The spectrum was obtained on a Shimadzu UV-200 spectrophotometer.
(24) NMR analyses were carried out with a Japan Electron Optics JNM-PS-100 spectrometer.

Chemical Purity and the Electrical Conductivity of Tetrathiafulvalinium Tetracyanoquinodimethanide

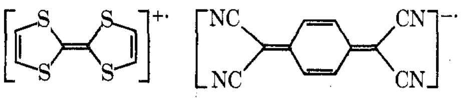
Robert V. Gemmer, Dwaine O. Cowan,* Ted O. Poehler, Aaron N. Bloch,[1] Ronald E. Pyle, and Rodney H. Banks

Department of Chemistry and The Applied Physics Laboratory, The Johns Hopkins University, Baltimore Maryland 21218

Received March 6, 1975

A critical evaluation using high-pressure liquid chromatography is made of three purification techniques for the neutral precursors of the highly conducting organic charge-transfer salt TTF-TCNQ (1). The purification techniques examined are (a) recrystallization, (b) sublimation, and (c) gradient sublimation. It is demonstrated that for the compounds studied gradient sublimation offers no significant advantage over more conventional sublimation techniques, and in fact is less efficient than simpler methods. Direct current conductivity data for crystals obtained from TTF^0 and TCNQ^0 of the varying purity are also presented. Only in extremely dirty samples do we see any significant change in electrical conductivity. We conclude that for impurity concentrations likely to be achieved routinely in most laboratories, crystal perfection rather than chemical purity chiefly determines the sample-dependent conductivity of TTF-TCNQ.

The best organic conductors of electricity known are the charge-transfer salt TTF-TCNQ (tetrathiafulvalinium tetracyanoquinodimethanide, 1), first prepared in these laboratories,[2-8] and several of its derivatives[9] and analogs.[10,11] The chain-like structures[5] of these materials lead to conductivities which are highly anisotropic, but metallic in magnitude along the chain axis. Since the propagation of conduction electrons is thus restricted effectively to one dimension, it is natural to expect chemical impurities and lattice defects to influence transport more profoundly here than in conventional three-dimensional metals.



1

Interest in the problem of purification has sharpened with the observation[2,12-14] that the conductivity of TTF-TCNQ is strongly sample dependent. Although it now appears that early reports[12] of truly giant conductivities in occasional crystals were overstated,[15-17] the variation among specimens is still large enough that the intrinsic conductivity of TTF-TCNQ remains in some doubt. Compounding the uncertainty are claims by at least one laboratory[12,13,18] of extreme chemical purity, based solely upon accounts of the methods of purification and care employed in synthesis.

Toward a resolution of these questions, we have undertaken to evaluate the methods currently used by various laboratories for purification of the neutral molecules TTF^0 and TCNQ^0. Using newly available techniques of high-pressure gel permeation chromatography, we obtain separations of 4000–5000 theoretical plates, and by differential ultraviolet detection we are able to monitor impurity concentrations as low as 1 ppm. We find that conventional techniques of recrystallization and sublimation are sufficient to reduce impurity levels in TTF^0 below the sensitivity of our instruments. The same is true of TCNQ^0 except for a tendency to complex weakly with acetonitrile. The acetonitrile is removed upon formation of the TTF-TCNQ salt. The gradient sublimation technique introduced by McGhie et al.[18] offers no improvement for TTF^0 or TCNQ^0. The conductivities of TTF-TCNQ crystals of maximum purity are the same as reported previously,[2,14,15] and not significantly different from those of deliberately contaminated samples. The latter, however, appear more susceptible to inhomogeneous current distributions which give rise to spurious giant apparent conductivities.[15,16] We conclude that most of the variation in conductivity among samples of TTF-TCNQ is due to lattice imperfections rather than chemical purity.

Results and Discussion

Three methods of purification were examined in this study: (a) recrystallization in an inert atmosphere using dry, purified solvents, (b) nonfractionating sublimation onto Teflon,[19] and (c) fractionating, or gradient sublimation onto Teflon.

A critical evaluation of these techniques was accomplished by the use of high-pressure liquid chromatography[20] (HPLC). Through the use of a differential uv detector operated at 254 nm, this method allowed detection of as little as 10^{-9} g, depending on the absorbtivity of the sample. The use of μ-styragel[21] gel-permeation[22] columns, which are capable of separating molecules of moderate molecular weights on the basis of effective size (including solvation sphere), gave chromatographs of both TTF^0 and TCNQ^0 which demonstrated the presence of characteristic impurities. In addition, these columns avoided the difficulties encountered when more conventional columns were used. For example, in the case of TTF^0, "normal phase" (i.e., liquid–solid absorption) HPLC proved to be unsatisfactory because of the low affinity of silica toward TTF^0. "Reverse phase" (i.e., liquid–liquid partition) HPLC using a permanently bonded hydrocarbon on silica phase gave satisfactory retention volumes for TTF^0 but proved useless owing to the sensitivity of TTF^0 to water (aqueous acetonitrile is required for the separation). Reverse phase HPLC was similarly unsatisfactory for TCNQ^0, as was normal phase owing to the possible presence of nonobservable highly polar impurities.

HPLC Analysis. For the analytical runs using TTF^0, recrystallized, sublimed, and gradiently sublimed TTF^0 (samples a, b, and c, respectively, see Experimental Section) were injected as approximately 0.5 *M* solutions in dry, deoxygenated THF. A solution of the starting material was prepared similarly. The resulting chromatographs are presented in Figures 1 and 2. (All figures appear as supplementary material in the microfilm edition. See paragraph at end of paper for details.) Figure 1 is the chromatography of the starting TTF^0. The Δuv traces are of particular interest. For the starting TTF, we note a significant impurity at a retention volume (RV) of 15 ml. This peak is due to a molecule *larger* than TTF^0, smaller compounds being eluted later owing to greater penetration of the gel pores. This impurity is essentially removed (Figure 2a) after three recrystallizations. After one sublimation onto Teflon using a vertical sublimator, we note that this impurity has, within the limits of detection, disappeared (Figure 2b). Thus it appears that recrystallization and a simple sublimation provide TTF^0 of excellent purity. Figure 2c demonstrates that gradient sublimation provides no advantage over the simpler method.

In contrast, gradient sublimation of TTF which has not been extensively recrystallized does not remove the small impurity present at RV 15 (Figure 3). Approximately the same amount of impurity was present before and after two gradient sublimations. Thus gradient sublimation of itself does not provide TTF^0 of exceptional purity, and can be exceeded in purifying ability by much simpler methods.

The analysis of TCNQ^0 was carried out essentially as that for TTF^0. A minor change was made owing to the low solubility of TCNQ^0 in THF. Since a saturated solution at room temperature was only about 0.01 *M*, injections of 100 μl were used. This did not cause any significant peak broadening.

The results of the analysis are presented in Figures 4 and 5. Figure 4 is a chromatograph obtained from the starting TCNQ^0. This material, which had been sublimed once, exhibited three extraneous peaks at RV 13.5, 18.5, and 20 ml. Multiple recrystallization under argon yielded material (Figure 4a) in which the impurities were somewhat reduced. Sublimation onto Teflon using the vertical sublimator yielded material (Figure 4b) from which essentially all of the impurities at RV 13.5 and 18.5 ml had been removed. The residual peak near RV 15 ml may be due to dihydro-TCNQ (*p*-bisdicyanomethylbenzene).[23] However, the peak at RV 20 ml had not been diminished significantly. Even gradient sublimation (Figure 4c) did not remove this impurity. Likewise, as in the case of TTF^0, gradient sublimation did not afford material significantly purer than a simpler sublimation method.

The persistence of the peak at RV 20 ml is particularly troublesome. For some reason the peak does not seem to be susceptible to removal by sublimation. Its composition can be inferred by reference to Figure 4. First of all, the impurity is smaller than TCNQ^0, being eluted very close to the totally included volume of the column (that is, the volume which includes all the accessible pores of the gel). Second, the relative intensities of the ΔRI and Δuv detector responses suggest a compound having an absorbence at 254 nm only slightly different from that of THF. In view of the above facts, a likely candidate is acetonitrile, the recrystallization solvent.[25] A reason for its persistence even during sublimation might be a weak charge-transfer interaction with TCNQ.[26] This hypothesis is supported by the observation of a typical –CN absorption at $\sim$2220 cm^{-1} in the ir spectrum of the peak at RV 20 ml. In addition, gas chromatographic and mass spectrometric evidence is consistent with the presence of acetonitrile. The presence of acetonitrile is sublimed TCNQ^0 presents a potential source of contamination in crystals of TTF-TCNQ. However, HPLC of crystals of the salt (which had been grown in acetonitrile) showed no evidence of the solvent, indicating at least a 20-fold decrease in the amount of acetonitrile present.

While certainty remains impossible, we feel strongly that no significant impurities have gone undetected in either TTF^0 or TCNQ^0. This statement is supported by three observations. The first is the high theoretical plate values[29] obtained for TTF^0 ($\sim$5000) and TCNQ^0 ($\sim$4000). Second, recycling the TTF^0 or TCNQ^0 peak in excess of five times provided no evidence for any impurities not observed in one pass through the columns. Third, HPLC traces obtained at wavelengths other than 254 nm (220, 280, 330, 450, and 500 nm) gave no evidence of new impurities. It is important to note at this point that the particular impurities present will in general depend on the method of preparation and handling of any given sample.

Conductivities. As a test of the importance of impurities in the TTF-TCNQ salt, we compared the conductivity of impure crystals to that of crystals grown under rigorously clean conditions. One of the reasons that other workers[12–14,18] claimed to have obtained extraordinarily pure TTF-TCNQ was their use of a quartz apparatus during crystal formation, thus reducing the possibility of leeching salts from borosilicate glass. In order to further reduce this possibility, we coated the interior of two inverted U-tube crystallizers with Teflon. We placed several crystals of NaCl in one of these to imitate the leeched salts. The other was kept clean. Crystals of the salt were grown by diffusion of acetonitrile solutions of gradiently sublimed TTF^0 and TCNQ^0. Crystals were also obtained from the starting TTF^0 and TCNQ^0.

The dc conductivities of representative "clean", "salty", and "dirty" crystals, measured by conventional four-probe techniques,[30] are summarized in Table I. No significant differences are observed among the three types of crys-

Table I

Crystal no.	Crystal type[a]	σ_{max},[b] 10^3 ohm^{-1} cm^{-1}	σ_{max}[b]/σ_{RT}	T_{max}, K
40	Salty	6.27	15.5	59
41	Salty	5.34	14.2	59
42	Clean	8.48	17.5	59
43	Clean	7.67	14.5	59
44	Clean	11.6	20.4	58
45	Salty	5.45	13.1	60
46	Clean	3.08	7.4	59
47	Clean	6.41	13.9	58
51	Clean	3.08	16.3	59
52	Clean	8.08	12.5	59
53	Clean	8.01	14.8	58
55	Salty	3.24	16.6	59
56	Salty	4.53	14.4	58
57	Salty	3.37	13.6	59
91	Dirty	3.53	9.6	65
95	Dirty	5.04	10.3	61
96	Dirty	5.80	16.5	58
97	Dirty	7.74	23.3	56
39	Salty	71.9[c,d]	120.[c,d]	59

[a] "Clean" indicates crystallization of TTF-c and TCNQ-c from CH_3CN in a Teflon-coated inverted U-tube. "Salty" indicates crystallization of TTF-c and TCNQ-c from CH_3CN containing NaCl in a Teflon-coated U-tube. "Dirty" indicates crystals obtained from the starting TTF^0 and $TCNQ^0$ using a glass apparatus. [b] Average values of σ_{max} taken as the temperature was decreased and then increased. [c] These results do not represent the true conductivity of this crystal. See text. [d] Value taken as the temperature was decreased. Upon warming this crystal exhibited two peaks, 3.4×10^5 ohm^{-1} cm^{-1} at 58 K and 1.3×10^5 ohm^{-1} cm^{-1} at 66 K.

tals.[31] However, a substantial variation in the ratio of the conductivity at the maximum to the room temperature conductivity (σ_{max}/σ_{RT}) is observed within each type; this we attribute to crystalline imperfections. Among the "dirty" crystals there is also considerable variation in the temperature at which σ_{max} occurs. Here the lowest conductivity peaks appear at the highest temperatures, consistent with previous observations.[13]

One crystal of the "salty" variety, no. 39, does not fit the generally consistent conductivity behavior we observed. This crystal was particularly large and apparently well formed. As the temperature was lowered, it displayed a single, sharp maximum in the apparent conductivity of 7.2×10^4 Ω^{-1} cm^{-1} (σ_{max}/σ_{RT} ~120) at 59 K. This behavior essentially duplicates that of the occasional crystals to which Coleman et al.[12] assigned giant intrinsic conductivities. In this case, however, continuous monitoring of the voltage checks suggested by Schaefer et al.[15] revealed the giant conductivity to be an artifact due to inhomogeneous current distributions. A detailed analysis of these results will be presented elsewhere.[16] With repeated thermal cycling the apparent σ_{max}/σ_{RT} rose to ca. 350, then rapidly deteriorated, with auxiliary conductivity maxima appearing at higher temperatures. The voltage checks continued to show that none of the cycles measured the true conductivity of the specimen.

Experimental Section

General. Gas chromatography was performed on a Hewlett-Packard Model 402 GC using a flame ionization detector. Two columns were employed: 5% UC-W98 on Chromosorb P and 10% Carbowax on Chromosorb W. Mass spectra were obtained on a Hitachi RMU-6 mass spectrometer operated at 70 eV.

All manipulations of the TTF^0 and $TCNQ^0$ samples were carried out under an argon atmosphere, using either dry Schlenk apparatus or glove bag techniques.[32] The purified samples were stored prior to analysis in argon-filled vials, under argon at −30°.

The solvents used were all dry and oxygen free. Acetonitrile (Burdick and Jackson spectrograde) was passed through 50 g of Super I Al_2O_3 (Woelm) and deoxygenated by bubbling argon through it for 15 min.[33] Petroleum ether (Fisher, bp 60–64°) was purified by shaking three times with concentrated H_2SO_4, distillation, and finally passage through Super I Al_2O_3, and deoxygenated using argon. Tetrahydrofuran (Fisher reagent grade) was purified by stirring with $LiAlH_4$ and then distilled under argon. All solvents were used immediately after purification.

Sublimations were carried out in two ways.

(1) Vertical Tube Sublimation. Into a sublimator consisting of a 25 × 1.5 cm tube fitted with a vacuum connection and lined with a piece of Teflon sheeting (5 × 20 cm) was placed a sample of TTF or TCNQ. The tube was placed on an efficient vacuum line in a vertical position and evacuated and then the lower 2 cm was heated using an oil bath. After the sublimation was judged complete, the tube was cooled and filled with Ar. The Teflon sleeve was taken out and the sublimate was removed for subsequent treatment.

(2) Gradient Sublimation. A gradient sublimation apparatus was constructed using as a model McGhie's[18] design. Vacuum connections were made via an O-ring high-vacuum seal and a high-vacuum Teflon stopcock to further reduce changes of contamination. For a typical run the apparatus was lined with a Teflon sheet (10 × 60 cm) fitted with a Teflon cap to assure that no glass surface was available to the substrate. After being dried with a flame under vacuum, the tube was filled with Ar and the sample was introduced via a Teflon boat. The apparatus was evacuated and placed in a gradient heater[18] which had been preequilibrated to the appropriate conditions. When the sublimation was complete, the tube was cooled and filled with argon and the sample was removed as above. Only that portion of the sublimate present as large crystals was collected.

Liquid Chromatography. The instrument used for the HPLC was a Waters Associates ALC-201 chromatograph fitted with a U-6K septumless injector. The detection system consisted of a differential refractive index detector followed by a differential uv detector operated at 254 nm. Two 30 cm long 100-Å μ-styragel columns were used. The eluting solvent was tetrahydrofuran, the flow rate was 1 ml/min, and the temperature was ambient. HPLC traces at wavelengths other than 254 nm were obtained using a Schoeffel Model SF770 spectroflow monitor coupled with a Model GM770 monochromator.

Purification. Tetrathiafulvalene. The starting material was prepared by coupling dithiolium perchlorate using triethylamine,[35] and had been recrystallized once from hexane (mp 119.1–119.5). TTF-a was obtained after three crystallizations from ligroin. TTF-b was obtained after vertical tube sublimation of TTF-a at 75°. Finally TTF-c was obtained from TTF-b by sublimation over a gradient of 80° to 25°. In each case a small amount of the sample was removed and stored under Ar at −30° before proceeding to the next step.

Tetracyanoquinodimethane. The starting material was obtained from Aldrich[39] and had been sublimed once in a conventional manner prior to use (mp 294–296°). TCNQ-a was prepared by recrystallization three times from acetonitrile. TCNQ-b was prepared from TCNQ-a by vertical sublimation at 155°. TCNQ-c was prepared from TCNQ-b by sublimation over a gradient of 150° to 100°. A small amount of each sample was removed and stored under Ar at −30° before proceeding to the next step.

HPLC Analysis. Samples for HPLC analysis were prepared by placing a small amount of each in a weighed vial fitted with a serum cap. Sufficient THF was injected into the vials to give, in the case of TTF^0, a 100 mg/ml solution. In the case of $TCNQ^0$, approximately 500 μl was injected into each vial. The prepared samples were kept in the dark under an Ar atmosphere prior to use. The analyses were carried out by injecting 15 μl of the TTF^0 solution or 100 μl in the cases of $TCNQ^0$. Repetitive injections were made to check the reproducibility of the chromatographic traces.

Complex Formation and Conductivity Measurements. The complex of TTF^0 and $TCNQ^0$ was formed by diffusive crystallization of their solutions in an inverted U-tube crystallizer. The crystallizers were Teflon coated by the following procedure.[41] The U-tube, scrupulously clean, was evacuated on an efficient vacuum line. After thorough flame drying, approximately 2 Torr of CF_2CF_2, obtained from the pyrolysis of Teflon chips, was introduced into the tube. Approximately 25 Torr of di-*tert*-butyl peroxide was then added, and the tube was isolated from the vacuum line and heated at 150° until a faint opalescence was apparent. Success of the procedure was determined by placing a drop of distilled water in the tube. If any surface was wetted, the process was repeated.

For the "salty" crystals, ca. 0.1 mg of reagent grade NaCl was placed in each side of the crystallizer.

Conductivity measurements were performed using standard four-probe techniques.[30]

Acknowledgments. This work was supported by a grant from the Materials Science Office, Advanced Research Projects Agency, Department of Defense. We wish to thank Dr. John P. Ferraris for the preparation of the TTF used in this work.

Registry No.—TTF-TCNQ, 40210-84-2; tetrathiafulvalene, 31366-25-3; tetracyanoquinodimethane, 1518-16-7.

Supplementary Material Available Figures 1–5, the HPLC traces, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-3544.

References and Notes

(1) Alfred P. Sloan Fellow.

(2) J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).

(3) J. H. Perlstein, J. P. Ferraris, V. Walatka, D. O. Cowan, and G. A. Candela, *AIP Conf. Proc.*, **10**, 1494 (1973).

(4) A. N. Bloch, J. P. Ferraris, D. O. Cowan, and T. O. Poehler, *Solid State Commun.*, **13**, 753 (1973).

(5) T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **30**, 763 (1974).

(6) T. O. Poehler, A. N. Bloch, J. P. Ferraris, and D. O. Cowan, *Solid State Commun.*, **15**, 337 (1974).

(7) M. A. Butler, J. P. Ferraris, A. N. Bloch, and D. O. Cowan, *Chem. Phys. Lett.*, **24**, 600 (1974).

(8) E. F. Skelton, A. N. Bloch, J. P. Ferraris, and D. O. Cowan, *Phys. Lett. A*, **47**, 313 (1974).

(9) J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Lett.*, 2553 (1973).

(10) K. Bechgaard, D. O. Cowan, and A. N. Bloch, *Chem. Commun.*, 937 (1974).

(11) E. M. Engler and V. K. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974).

(12) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).

(13) M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **10**, 1298 (1974).

(14) R. P. Groff, A. Suna, and R. E. Merrifield, *Phys. Rev. Lett.*, **33**, 418 (1974).

(15) D. E. Schaefer, F. Wudl, G. A. Thomas, J. P. Ferraris, and D. O. Cowan, *Solid State Commun.*, **14**, 347 (1974).

(16) D. E. Schaefer, G. A. Thomas, R. E. Pyle, R. Banks, A. N. Bloch, R. V. Gemmer, and D. O. Cowan, to be published.

(17) A. N. Bloch, V. Walatka, Jr., D. O. Cowan, T. O. Poehler, Y. Tomkiewicz, and D. Garrod, to be published.

(18) A. R. McGhie, A. F. Garito, and A. J. Heeger, *J. Cryst. Growth*, **22**, 295 (1974).

(19) Registered trademark, E. I. du Pont de Nemours and Co.

(20) J. J. Kirkland, Ed., "Modern Practice of Liquid Chromatography", Wiley, New York, N.Y., 1972.

(21) Registered Trademark, Waters Associates, Milford, Mass.

(22) (a) G. Determann, *Adv. Chromatogr.*, **8**, 3 (1969); (b) K. J. Bombaugh in ref 20, Chapter 7.

(23) This possibility, suggested by J. D. Wilson, Monsanto Corp., is supported by the observation that dihydro-TCNQ (mp 243–245°), prepared by treating TCNQ with aqueous HI,[24] elutes at RV 15.2 ml under the conditions used for our analysis.

(24) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

(25) Recrystallization from other solvents (e.g., ethyl acetate) removed this peak. However, acetonitrile was retained as the recrystallization solvent on the basis of its effectiveness in removing other impurities.

(26) Acetonitrile is known to act as a donor with halogens[27] and aromatic hydrocarbons.[28]

(27) A. I. Popov and W. A. Deskin, *J. Am. Chem. Soc.*, **80**, 2976 (1958); W. B. Pearson, W. C. Golton, and A. I. Popov, *ibid.*, **85**, 981 (1963).

(28) J. V. Hatton and R. E. Richards, *J. Mol. Phys.*, **5**, 139 (1962); L. F. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(29) B. L. Karger, ref 20, p 16.

(30) V. Walatka and J. H. Perlstein, *Mol. Cryst. Liq. Cryst.*, **15**, 269 (1971).

(31) The low temperature (4.2 K) dielectric constant (at 10 GHz) was about 1000 for all samples, somewhat higher than we had reported earlier (see ref 4).

(32) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.

(33) Acetonitrile prepared in this manner is routinely used as a solvent for the electrochemical generation of sensitive dications.[34]

(34) C. LeVanda, D. O. Cowan, and K. Bechgaard, *J. Am. Chem. Soc.*, **97**, 1980 (1975).

(35) S. Hünig, G. Kiesslick, H. Quast, and D. Schneutzow, *Justus Liebigs Ann. Chem.*, **766**, 310 (1973). This is not a recommended procedure, as the perchlorate may explode.[36] Other salts may be used, however, including the hydrosulfate[37] and the fluoroborate.[38]

(36) J. P. Ferraris and F. I. Mopsik, *Chem. Eng. News*, 3 (Sept 16, 1974).

(37) (a) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garret, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971); (b) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1453 (1970).

(38) F. Wudl, M. L. Kaplan, E. J. Hufnagel, and E. W. Southwick, Jr., *J. Org. Chem.*, **39**, 3608 (1974).

(39) TCNQ from Aldrich is not qualitatively different by HPLC from unpurified TCNQ prepared[40] in our laboratories.

(40) J. P. Ferraris, Ph.D. Thesis, The Johns Hopkins University, 1973.

(41) D. M. Golden, Stanford Research Institute, private communication.

Barriers to Amide Rotation in Piperidides and Related Systems. Unambiguous Assignments Using Carbon-13 Magnetic Resonance

Jerry A. Hirsch,*[1a] Robert L. Augustine,[1b] Gabor Koletar,[1b,c] and Harold G. Wolf[1b,c]

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079, and the Gorlaeus Laboratories, Department of Organic Chemistry, P.O. Box 75, University of Leiden, The Netherlands

Received June 6, 1975

Variable-temperature carbon-13 magnetic resonance is used to investigate barriers to amide rotation in a series of benzoyl- and carboethoxy-substituted six-membered nitrogen heterocycles. Observed barriers are unambiguously assigned to amide rotation (as opposed to ring reversal or nitrogen inversion) because of the symmetry properties inherent in the carbon-13 technique. Barriers are compared with those obtained by variable-temperature proton magnetic resonance. The amide rotation barriers are relatively insensitive to changes in the nature of the ring substituent γ to the nitrogen, thereby supporting earlier results which suggested little or no 1,4-transannular interaction in six-membered heterocycles.

Application of carbon-13 magnetic resonance spectroscopy (^{13}C NMR)[2] to temperature-dependent phenomena (^{13}C DNMR) is still in its infancy.[2,3] It is the intention herein to use ^{13}C DNMR to provide unambiguous assignment of the nature of a dynamic process in a situation where several processes may occur. Variable-temperature proton magnetic resonance spectroscopy (^{1}H DNMR)[4] will be used to support[5] ^{13}C DNMR studies[6] in two examples.