

be experimentally distinct; in procedures C1 and C4, generation of the cation automatically gives the correct anion, thereby combining steps i and ii. The C procedures presumably all proceed by this process, but the two-phase systems are potentially mechanistically complex. Some of the betylates, for example, may act as phase transfer agents thereby making it difficult to distinguish between (a) substrate phase transfer (with the actual reaction occurring in the aqueous phase), and (b) "normal" phase transfer of the anion followed by a substrate-reagent ion-pair reaction in the organic phase; micellar and interfacial processes can also further complicate the picture.

Both the phase transfer and ion-pair processes are obviously capable of extension well beyond the betylate reactions given here, and we foresee application of betylate chemistry and of these methods not only in synthesis but in mechanistic and biological studies as well.

Acknowledgment. We thank the National Research Council of Canada for support of this work.

Supplementary Material Available: Preparation and use of betylates (3 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.
- (2) Presented at the CIC/ACS Joint Conference, Montreal, May–June, 1977.
- (3) So-called from their formation of betaines **2** on substitution or elimination.
- (4) Further experimental details regarding the preparation and use of betylates appear in the microfilm edition. See paragraph at end of paper regarding supplementary material.
- (5) In a three-step process, ROH \rightarrow **3** \rightarrow **4** (Nu = NMe₂) \rightarrow **1** ($n = 2$), taking typically ~1–2 h for 1–100 mmol quantities: J. F. King and S. M. Loosmore, *J. Chem. Soc., Chem. Commun.*, 1011 (1976). The synthesis of methyl [2]betylato perchlorate (**1**, $n = 2$; R = CH₃; X⁻ = ClO₄⁻) along with 15 other methyl and two ethyl esters of quaternary ammonium sulfonic acids has been described by P. Blumbergs, A. B. Ash, F. A. Danilher, C. L. Stevens, H. O. Michel, B. E. Hackley, Jr., and J. Epstein, *J. Org. Chem.*, **34**, 4065 (1969). These authors demonstrate clearly the utility of these species as water-soluble alkylating agents, but their method lacks the generality as well as the favorable yields and the ease and mildness of our procedures. A recent report also notes the hydrophilic and good leaving group properties of "amsylates" (trimethylammonium benzenesulfonates): C. N. Sukenik and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 6613 (1976).
- (6) R. K. Crossland, W. E. Wells, and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **93**, 4217 (1971).
- (7) Compound **5** is prepared by reaction of *N*-methyl propanesultam⁸ with excess MeOSO₂F at room temperature (J. R. du Manoir, unpublished observation).
- (8) A. D. Bliss, W. K. Cline, C. E. Hamilton, and O. J. Sweeting, *J. Org. Chem.*, **28**, 3537 (1963).
- (9) These methods are clearly distinguished from current general methods such as phase transfer catalysis or the use of mixed or dipolar aprotic solvent systems in that the latter focus on alteration of the reagent or the medium rather than the substrate.

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Mixed Phenazine-*N*-Methylphenazinium 7,7,8,8-Tetracyano-*p*-quinodimethanide. A Quasi-One-Dimensional "Metal-Like" System with Variable Band Filling

Sir:

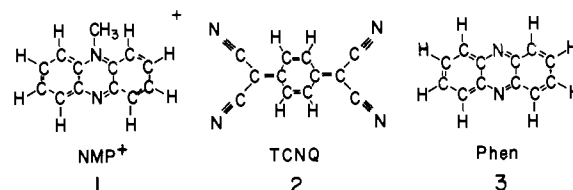
In the past few years there has been enhanced activity in the design and synthesis of highly conducting pseudo-one-dimensional (1-D) organic^{1,2} and inorganic complexes^{2,3} so that the salient features of such 1-D materials can be understood.⁴ To date only a few prototype organic systems have been studied. These are based on 7,7,8,8-tetracyano-*p*-quinodimethanide (TCNQ⁻) (**2**) salts of heterocyclic open shell sulfur

Table I. Unit Cell Parameters for (NMP)_x(Phen)_{1-x}TCNQ

	(NMP) (TCNQ) ^a	(NMP) _{0.74} ⁻ (Phen) _{0.26} ⁻ TCNQ	(NMP) _{0.54} ⁻ (Phen) _{0.46} ⁻ TCNQ
<i>a</i> , Å	3.8682 (4)	3.890 (8)	3.865 (7)
<i>b</i> , Å	7.7807 (8)	7.799 (3)	7.611 (32)
<i>c</i> , Å	15.735 (2)	15.706 (6)	16.329 (51)
α	91.67 (1)	91.75 (6)	93.73 (49)
β	92.67 (1)	92.96 (13)	91.53 (31)
γ	95.38 (1)	95.45 (2)	94.65 (20)
<i>V</i> , Å ³	470.7	473.4	477.4

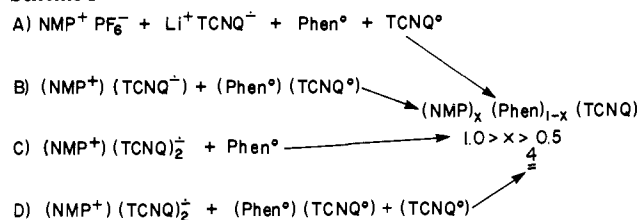
^a Reference 19.

(and/or selenium) (e.g., tetrathiofulvalene (TTF)), and closed shell nitrogen containing (e.g., *N*-methylphenazinium (NMP⁺, **1**) cations. The results of such studies and, in par-



ticular, the former open shell cation, TTF, has led to significant advances in the understanding of the physics of 1-D organic materials. However, many fundamental questions still persist. Since the charge-transfer organic 1-D complexes studied to date differ in structure and stoichiometry, comparisons between them have to be reported with caution. To alleviate the intrinsic comparative difficulties, we attempted to design an isomorphous series of highly conducting 1-D organic complexes which possess a variable filled conduction band so that the physical properties could be studied as a function of band filling, i.e., Fermi energy.⁵ Of the available prototype organic 1-D "metals", (NMP⁺)(TCNQ⁻)⁶ was chosen as the model system.^{7,8} It seemed reasonable that, if the TCNQ chain provides a driving force for the stabilization of the 1-D structure and if on the average each TCNQ in (NMP⁺)(TCNQ⁻) is TCNQ¹⁻, removal of NMP⁺ (and of course the electron associated with its TCNQ⁻ moiety) would reduce the average charge per TCNQ, i.e., TCNQ^{z-} ($z < 1$). Removal of the cation would destroy the unit cell; however, substitution of the NMP⁺ cation with a neutral molecule of comparable size, shape, and polarizability should stabilize the structure.¹⁰ For these reasons the substitution of phenazine, Phen (**3**), for NMP⁺ in (NMP⁺)(TCNQ⁻), (**1**)(**2**), was attempted.

Scheme I



Through reactions A, B, C, or D, outlined in Scheme I, complexes of (NMP⁺)_x(Phen)_{1-x}(TCNQ⁻)_x(TCNQ⁰)_{1-x} \equiv (NMP⁺)_x(Phen)_{1-x}(TCNQ)^{x-}, **4**, stoichiometry with $1 \geq x \geq 0.5$, could be isolated as dark reflecting needle crystals. Visual appearance and crystallographic, elemental composition and differential scanning calorimetry (DSC) measurements, as well as temperature dependence of the conductivity and magnetic susceptibility, indicate that these crystals resemble but are not identical with (NMP⁺)(TCNQ⁻).¹²

Unit cell determinations were obtained on **4** ($x = 0.24 \pm 0.01$ and 0.46 ± 0.01).¹⁸ The results suggest that **4** ($x = 0.24$

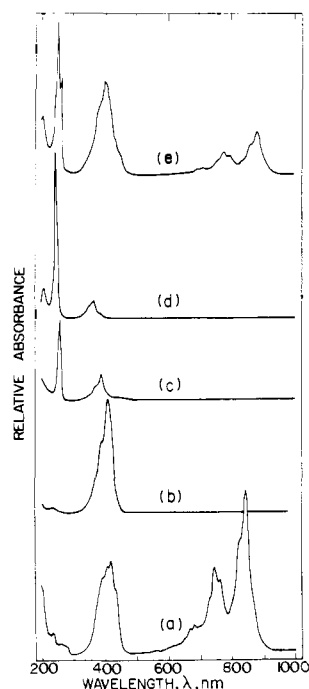


Figure 1. The absorption spectra of Li^+TCNQ^- (a), TCNQ^0 (b), $\text{NMP}^+\text{PF}_6^-$ (c), phenazine (d), and $(\text{NMP})_{0.54}(\text{Phen})_{0.46}(\text{TCNQ})$ (e). The ordinate is arbitrary.

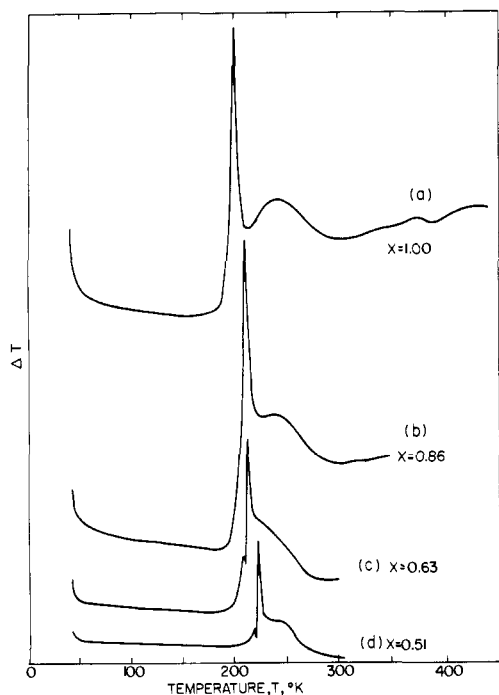


Figure 2. Differential scanning calorimetry traces of $(\text{NMP})_x(\text{Phen})_{1-x}\text{TCNQ}$ as a function of x .

and 0.46) is isomorphous to that reported by Fritchie¹⁹ for $(\text{NMP})(\text{TCNQ})$, Table I. The large standard deviations are an artifact of the small crystals utilized and broad ω scans¹⁸ which are characteristic of disorder.²⁰

Evaluation of the composition of **4**, i.e., x , was carried out by elemental analysis (which verifies that the $(\text{NMP}^+ + \text{Phen})/\text{TCNQ}$ ratio was 1:1 within elemental error) and electronic absorption spectra ($\sim 10^{-4}$ M in acetonitrile).²¹ Figure 1 shows the electronic absorption spectra of TCNQ^- (a), NMP^+ (b), Phen (c), TCNQ^0 (d), and $(\text{NMP}^+)_x(\text{Phen})_{1-x}(\text{TCNQ})^-_x(\text{TCNQ})_{1-x}$ for $x = 0.54$, **5** (e). The 46% replacement, i.e., $x = 0.54$, of Phen for NMP^+ in **5** is

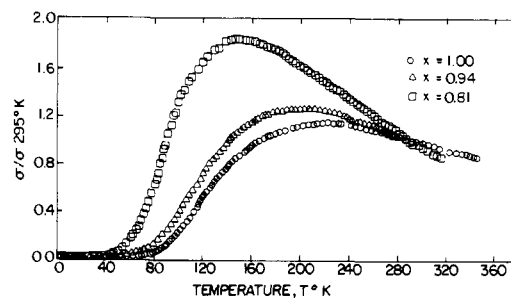


Figure 3. The temperature dependences of the conductivity for $(\text{NMP})_x(\text{Phen})_{1-x}\text{TCNQ}$ ($x = 1.00, 0.94, \text{ and } 0.81$).

calculated from the evaluation of the absorbance, A , of the 842-nm absorption,^{14,21} and the sample weight via

$$\begin{aligned} \% \text{TCNQ}^- &= \frac{w_{\text{TCNQ}^-}(\text{obsd})}{w_{\text{sample}}} \\ &= \frac{(x)\text{MW}_{\text{TCNQ}^-}}{(x)\text{MW}_{\text{NMP}^+} + (1-x)\text{MW}_{\text{Phen}} + \text{MW}_{\text{TCNQ}^-}} \quad (1a) \end{aligned}$$

where MW is the molecular weight, V and w are the sample volume and weight, respectively, and b and ϵ are the path length and molar extinction coefficient and

$$x = \frac{384.40z}{204.19 - 15.04z} \quad \text{with } z = \frac{A(\text{MW}_{\text{TCNQ}^-})V_{\text{sample}}}{b\epsilon_{842}} \quad (1b)$$

The spectra, as illustrated in Figure 1, show that **5** exhibits absorptions characteristic of Phen ($\lambda_{\text{max}} 347.5$ nm), NMP^+ ($\lambda_{\text{max}} 259$ nm), TCNQ ($\lambda_{\text{max}} 394$ nm), and TCNQ^- ($\lambda_{\text{max}} 842$ nm). Attempts to solve four simultaneous equations for the concentrations of each of the four species in solution were thwarted by the failure of the mixture to obey the Beer-Lambert law below 600 nm.

Complex **4** exhibited a DSC trace characteristic of that of $(\text{NMP}^+)(\text{TCNQ}^-)$. Unlike $(\text{Phen})(\text{TCNQ})$ ¹³ and $(\text{NMP}^+)(\text{TCNQ})_2^-$,¹⁴ **4** exhibits an exothermic decomposition at ≥ 200 °C. For larger x , the decomposition exotherm occurs at higher temperature. A new exothermic feature at ~ 5 – 15 °C lower temperature than the exotherm also appears with a magnitude which increases with x . Figure 2 depicts several DSC traces for **4** as a function of x .

An attempt to replace NMP^+ in $(\text{NMP}^+)(\text{TCNQ})_2^-$, **6**, with Phen via reaction D led to the isolation of **6** for small amounts of added Phen and **4** for larger amounts of Phen.

The dc electrical conductivity, σ , of **4** is also similar but not equivalent to that of $(\text{NMP}^+)(\text{TCNQ}^-)$,²² Figure 3. The "metal-like" behavior, i.e., $d\sigma/dT < 0$, is observed for all of the samples measured near room temperature. The characteristics of the conductivity and magnetic susceptibility which will be reported in full at a later time are (1) the temperature at which the maximum conductivity is achieved decreases with x ; (2) the $\sigma_{\text{max}}/\sigma_{\text{RT}}$ ratio increases with decreasing x ; and, finally, (3) the conductivity data for **4** ($1.0 > x > 0.5$) can be fit to the previously reported temperature dependent mobility model.²²

The details of the ac and dc conductivity, magnetic susceptibility, ESR, and thermoelectric power, as well as other measurements, will be reported later.

References and Notes

- (1) (a) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974); (b) M. Narita and C. U. Pittman, *Synthesis*, **8**, 489 (1976); (c) B. P. Bespalov and V. V. Titov, *Russ. Chem. Rev.*, **44**, 1091 (1975); (d) J. J. André, A. Bieber, and F. Gaultier, *Ann Phys. (Paris)*, **1**, 145 (1976); (e) A. N. Bloch, D. O. Cowan, and T. O. Poehler in "Energy and Charge Transfer in Organic Semiconductors", K. Masuda and M. Silver, Ed., Plenum Press, New York, N.Y., 1974, pp 167–176; (f) E. P. Goodings, *Chem. Soc. Rev.*, **5**, 95 (1976); (g) L. Pál, G. Grüner, A. Jánossy, and J. Sólyom, Ed., *Lect. Notes Phys.*, **65**

- (1977).
- (2) (a) H. J. Keller, Ed., *NATO Adv. Study Inst. Ser., Ser. B*, **25** (1977); (b) H. J. Keller, Ed., *NATO Adv. Study Inst. Ser., Ser. B*, **7** (1975); (c) L. V. Interrante, Ed., *ACS Symp. Ser., No. 5* (1975); (d) H. G. Schuster, Ed., *Lect. Notes Phys.*, **34** (1975).
- (3) (a) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976), and references therein; (b) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972).
- (4) (a) I. F. Shchegolev, *Phys. Status Solidi A*, **12**, 9 (1972); (b) A. J. Berlinsky, *Contemp. Phys.*, **17**, 331 (1976); (c) H. R. Zeller, *Festkoerperprobleme*, **13**, 31 (1973).
- (5) Scaling as a function of Fermi energy has been reported for $(\text{TTF}(\text{SCN})_{0.54})$, $(\text{TTF})(\text{SeCN})_{0.54}$, and $(\text{TTF})(\text{I})_{0.71}$: G. A. Thomas, F. Wudl, F. DiSalvo, W. M. Walsh, Jr., L. W. Rupp, and D. E. Schafer, *Solid State Commun.*, **20**, 1009 (1976).
- (6) Z. G. Soos, "Highly Conducting Organic Materials", accepted for publication.
- (7) $\text{TTF}^{0.59+}\text{TCNQ}^{0.59-}$ is extremely difficult to modify the band filling of since both cation and anion are redox active. Alloys of $(\text{TTF})(\text{TCNQ})$ with selenium analogues of TTF have been reported, though variation of band filling over the alloy range appears to be small: P. M. Chaikin, J. F. Kwak, R. L. Greene, S. Etemad, and E. M. Engler, *Solid State Commun.*, **19**, 1201 (1976); Y. Tomkiewicz, E. M. Engler, and T. D. Schultz, *Phys. Rev. Lett.*, **35**, 456 (1975); S. Etemad, *Phys. Rev. B*, **13**, 2254 (1976). See also M. L. Khidekél and E. B. Yagubskii, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1123 (1975); E. M. Engler, R. A. Craven, Y. Tomkiewicz, B. A. Scott, K. Bechgaard, and J. R. Andersen, *J. Chem. Soc., Chem. Commun.*, 337 (1976).
- (8) Substances have been reported where donors of similar charge and shape have been blended over a range of compositions.⁹ This, of course, does not alter the degree of band filling.
- (9) J. D. Wright, T. Ohta, and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **49**, 2961 (1976); S. Koizumi and Y. Matsunga, *ibid.*, **47**, 9 (1974); S. K. Lower, *Mol. Cryst. Liq. Cryst.*, **5**, 363 (1969); Y. Iida, *J. Phys. Chem.*, **80**, 2944 (1976).
- (10) The electrostatic contribution to the binding energy of $(\text{NMP}^+)(\text{TCNQ}^-)$ will increase with the addition of phenazine owing to reduction of repulsion between nearest neighbors within a stack.¹¹
- (11) A. J. Epstein, N. O. Lipari, D. J. Sandman, and P. Nielsen, *Phys. Rev. B*, **13**, 1569 (1976).
- (12) Complex **4**, however, does not visually, crystallographically, elemental compositionally, or via DSC traces resemble $(\text{Phen})(\text{TCNQ})$,¹³ $(\text{NMP}^+)(\text{TCNQ})_2$,¹⁴ $(\text{NMP}^+)(\text{TCNQ}^-)$, phase II¹⁵ recently shown to be $(\text{HNMP}^+)(\text{TCNQ})$,¹⁶ or $(\text{NMP}^+)_2(\text{TCNQ})_3$.¹⁷
- (13) I. Goldberg and U. Shmueli, *Nature*, **234**, 36 (1971).
- (14) L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965).
- (15) L. B. Coleman, S. K. Khanna, A. F. Garito, and A. J. Heeger, *Phys. Lett. A*, **42**, 15 (1972); B. Morosin, *Acta Crystallogr., Sect. B*, **32**, 1176 (1976).
- (16) Z. G. Soos, private communication.
- (17) S. Sanz and J. J. Daly, *J. Chem. Soc., Perkin Trans. 2*, 1146 (1975).
- (18) Molecular Structure Corporation, College Station, Texas.
- (19) C. J. Fritchie, Jr., *Acta Crystallogr.*, **20**, 892 (1966).
- (20) Disorder has been previously reported for $(\text{NMP})(\text{TCNQ})$: B. Morosin, *Phys. Lett. A*, **53**, 455 (1975); H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 1373 (1975).
- (21) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).
- (22) A. J. Epstein, E. M. Conwell, D. J. Sandman, and J. S. Miller, *Solid State Commun.*, **23**, 355 (1977).

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Book Reviews

Electronic Structure and Magnetism of Inorganic Compounds. Volume 4. By P. DAY (University of Oxford). The Chemical Society, London. 1976. ix + 277 pp. \$45.50.

This volume in the series contains four chapters on Electronic Spectra, Magnetic and Natural Optical Activity, Magnetic Susceptibility Measurement and, new this year, Luminescence Properties of Inorganic Compounds. The high standards of previous volumes are more than met by Volume 4. The coverage of the literature, primarily for 1973, appears comprehensive. The three-year delay between the time the work appears in the journals and the publication of this work is unfortunate but probably unavoidable. Particularly appreciated by this reviewer is the range of topics covered in most chapters including monographs and reviews as well as journal articles, on theory, experimental techniques and instrumentation, and results. The writing is concise yet still very readable and relatively free of typographical errors. The authors have understandably but regrettably limited critical analysis of results and conclusions to a small number of cases. When they have chosen to comment their remarks are very useful. All in all this is an excellent piece of work and the authors deserve much credit for a massive undertaking so well done.

W. A. Baker, *The University of Texas at Arlington*

Carbohydrate Chemistry. Volume 8. Senior Reporter: J. S. BRIMCOMBE (University of Dundee). The Chemical Society, Burlington House, London. 1976. 485 pp. \$66.00.

This is another of the Specialist Periodical Reports and covers the literature available to the group of seven reporters from mid-January 1974 to mid-January of 1975 in admirable fashion. Part I, concerned with mono-, di-, and trisaccharides and their derivatives, contains 27 chapters on such topics as amino sugars, ethers, cyclitols, glycosides, nucleosides, NMR spectroscopy, and conformational analysis. Articles dealing with microbial polysaccharides, enzymes, glycoproteins, and glycolipids are among the eight chapters concerned with macromolecules in Part II. There are more than 3100 references (mainly to papers published in 1973 and 1974), and many useful diagrams. The reporters have managed the difficult task of presenting indepth coverage of an impressive number of topics in a clear and concise manner. The reviews demand considerable background from the reader; they

should be valuable to the research worker, to the faculty member wishing to organize a course, and to anyone interested in really digging into this area. Ideas for further research turn up continually. A detailed list of contents helps to compensate for the lack of an index. Volume 8 is a stimulating and detailed account of advances in carbohydrate chemistry during the period surveyed.

Robert A. Weisman, *Wright State University*

Beam-Foil Spectroscopy. Edited by S. BASHKIN (University of Arizona). Springer-Verlag, Berlin-New York. 1976. xiv + 318 pp. \$28.30.

This book presents a remarkably complete introduction to and survey of the current status of beam-foil spectroscopy (BFS). It consists of ten chapters by eleven different authors, all of whom are recognized authorities on BFS. Bashkin's introductory chapter on experimental methods in BFS sets the tone for the remainder of the book—a lucid presentation rich in information about BFS. Topics covered include hydrogenic and multiply-excited levels populated in BFS; mean life measurements utilizing BFS; oscillator strengths; applications of BFS in astrophysics; Lamb shift and forbidden decay studies; coherence, alignment and orientation of the BFS source; and fast projectile electron spectroscopy via beam-foil excitation. Throughout the book, care is taken to balance the experimental discussions with theoretical calculations. The relative advantages and disadvantages of BFS compared to other methods of obtaining information about monatomic systems are also discussed. Ample suggestions for BFS studies remaining to be made are sprinkled throughout the book. Perhaps the strongest point of this work is the extensive reference list provided at the end of each chapter and in the appendix. These alone make this book an excellent source work on BFS.

Arlen R. Zander, *East Texas State University*

Physicochemical Methods of Mineral Analysis. Edited by A. W. NICOL (University of Birmingham, England). Plenum Press, New York, N.Y. 1975. xv + 508 pp. \$34.80.

The book originated from a university course in England which presented an account of new physicochemical methods applicable in