showed that solutions of CuL_2 in CCl_4 are most susceptible to photolysis and those in benzene least susceptible, (the other usual extractants falling between these two limits), these two solvents were chosen for a detailed study.

Studies in Diffused Day-light

Known volumes of these solutions were taken in clear-glass stoppered bottles and were exposed to diffused day-light for different periods. Measured aliquots were removed at definite time intervals and their absorbance was determined at 435 nm. (CuL_2 has a characteristic absorption peak at 435 nm due to a ligand-to-metal charge transfer band.) It was found that CCl_4 solutions deteriorated fast, whereas benzene solutions appeared to be much stabler. For instance, after a 4 hour exposure to diffused day-light, the absorbance of a typical solution fell from an initial value of 0·490 to 0·340 in CCl_4 medium, while in a benzene medium, it dropped from 0·490 only to 0·475.

Studies Using a Mercury Arc Lamp

A low pressure mercury arc lamp (Hanovia, 4 Watts, 220 volts) and a water-cooled quartz photochemical cell with an inner thimble (capacity 1 litre) were used. Standard CuL_2 solutions were irradiated at two temperatures, $30° \pm 0·1$ and $36° \pm 0·1$. The results indicated that temperature variations, as above, have practically no effect on the decomposition rate. The results of a typical study at 30° are given in Table I.

TABLE I

Photochemical decomposition of CuL_2 using 4 Watts UV lamp

Time hours	Absorbance in CCl_4	Absorbance in benzene
0	2·060	2·120
0·5	1·960	2·090
1·0	1·855	2·070
1·5	1·700	2·040
2	1·501	2·010
3	1·344	2·000
4	1·074	1·990
5	1·038	1·970
6	0·859	1·960
8	0·830	1·910
12	0·650	1·840
16	0·286	1·820
20	0·120	1·770
24	0·096	1·665

CCl_4: $k = 3·57 \times 10^{-5}$ sec^{-1}; $\phi = 0·081$; $t_{\frac{1}{2}} = 5·4$ hours. Benzene: $k = 2·99 \times 10^{-6}$ sec^{-1}: $\phi = 0·0073$; $t_{\frac{1}{2}} = 64·4$ hours.

The progress of the substrate disappearance was followed by withdrawing small measured aliquots (2 ml) at definite time intrervals, diluting to 10 ml and determining the absorbance values (A) at 435 nm. Since the volume of the aliquot removed (2 ml) is very small in comparison with the volume of the system (1000 ml), the volume effect is ignored in the present study. A plot of log (A_0/A_t) against time (t) was found to be a straight line both in CCl_4 and in benzene, where A_0 and A_t denote absorbance at $t = 0$ and $t = t$. This implies conformity with the first order kinetics. The rate constant for substrate disappearance (k) was found to be $3·57 \times 10^{-5}$ sec^{-1} in CCl_4 and $2·99 \times 10^{-6}$ sec^{-1} in benzene. The values for the time of half change are: $t_{\frac{1}{2}} = 5·4$ hr in CCl_4 and $t_{\frac{1}{2}} = 64·4$ hr in benzene. An increase of temperature from 30° to 36° did not significantly affect the value of k. A preliminary determination of the average quantum efficiency of the decomposition gave values of $\phi = 0·081$ in CCl_4 and $\phi = 0·0073$ in benzene.

It was observed that a solid residue was thrown down in the CCl_4 medium during the course of the decomposition. This is analysed for Cu^{2+}, Cl^- and elemental sulphur. The decomposition reaction thus appears to be complicated, as is the case with several photolytic reactions of co-ordination complexes[4].

From these studies, it is clear that benzene is a better solvent than CCl_4 for the spectrophotometric determination of copper.

We are grateful to Council of Scientific and Industrial Research for the award of a Junior Fellowship to one of us (K. K. M. Y.).

Dept. of Chemistry, Kerala University, Trivandrum 695001, *September* 21, 1974.

K. K. MOHAMMED YUSUFF.
P. M. MADHUSUDANAN.
C. G. RAMACHANDRAN NAIR.

1. Callan, T. and Henderson, J. A. R., *Analyst*, 1929, 54, 650.
2. Nair, C. G. R., Rao, V. R. S. and Murthy, A. R. V., *Mikrochim. Acta*, 1961, p. 741.
3. Waltz, W. L. and Sutherland, R. G., *Chem. Soc. Rev.*, 1972, 1, 241.
4. Balzani, V. and Carassiti, V., *Photochemistry of Coordination Compounds*, Academic Press, London, 1970.

MESOMORPHIC PROPERTIES OF SOME BIPHENYL BENZOATES

SEVERAL biphenyl esters exhibit mesomorphic properties[1,2]. As a part of our programme of study of the structure and properties of liquid crystals, we have synthesized a homologous series of ten biphenyl-4-*p*-*n*-alkoxybenzoates starting from *p*-*n*-

alkoxybenzoic acids through their acid chlorides. The transition temperatures and elemental analyses are given in Tables I and II respectively.

TABLE I

Transition temperatures of biphenyl 4-p-n-alkoxy benzoates

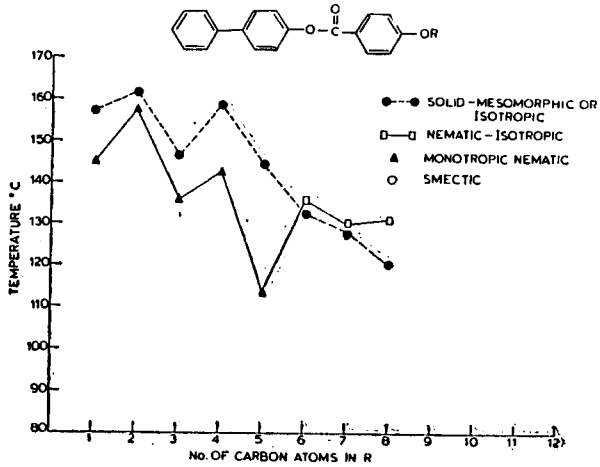
Compound number	R[a]	Transition temperatures °C			△ T °C nematic range
1	CH_3	157	−157·5	(145)	..
2	C_2H_5	161	−162	(157·5)	..
3	C_3H_7	146	−147	(136)	..
4	C_4H_9	158	−159	(142·5)	..
5	C_5H_{11}	144	−145	(113·5)	..
6	C_6H_{13}	132·5	−135·5		3
7	C_7H_{15}	128	−130		2
8	C_8H_{17}	120	−131		11
9	$C_{10}H_{21}$	111	−126·5	(106) S	15·5
10	$C_{12}H_{25}$	110·2 S	= 113·2 −	124·5	11·3

[a] All alkyl (R) groups are normal. Temperatures in parentheses indicate monotropic transitions. S indicates the occurrence of a smectic phase.

TABLE II

Compound number	Molecular formula	Calculated % C	Calculated % H	Found % C	Found % H
1	$C_{20}H_{16}O_3$	78·94	5·262	78·78	5·50
2	$C_{21}H_{18}O_3$	79·25	5·661	79·52	5·763
3	$C_{22}H_{20}O_3$	79·52	6·024	79·50	6·280
4	$C_{23}H_{23}O_3$	79·77	6·357	79·64	6·45
5	$C_{24}H_{24}O_3$	80·00	6·766	80·00	6·94
6	$C_{25}H_{26}O_3$	80·21	6·952	80·19	7·18
7	$C_{26}H_{28}O_3$	80·42	7·218	80·55	7·57
8	$C_{27}H_{30}O_3$	80·60	7·463	80·22	7·63
9	$C_{29}H_{31}O_3$	81·08	8·108	81·14	7·98
10	$C_{31}H_{38}O_3$	81·21	8·296	81·32	8·28

The first five members of the series exhibit a monotropic nematic mesophase. The hexyl, heptyl, and octyl derivatives are enantiotropic nematic. The smectic mesophase appears at the decyl derivative as a monotropic phase. The plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain is given in Fig. 1, and shows the usual odd-even effect. The thermal stability of the nematic phase decreases with increasing carbon chain length. It is interesting to note that there is alternation in the crystal to isotropic transition temperatures of the first five members of the series. This alternation is attributed to a similarity in crystal structure, as evidenced from the X-ray study[3] of the higher homologues of *p-n*-alkoxybenzoic acids. These esters are thermally less stable than the corresponding Schiff's bases reported by Gray *et al.*[4].



The transition temperatures were determined in open capillary tubes using a polarizing microscope (Franz Kustner Nacht KG, Dresden, Model HMK 70/3171) in conjunction with a heated stage. Infrared spectra were recorded (nujol mull) on a Perkin-Elmer spectrophotometer, Model 700 and NMR spectra were recorded on a Varian T-60 spectrometer, in $CDCl_3$ using tetramethylsilane as internal standard. The *p-n*-alkoxybenzoic acids were prepared according to the method of Lauer *et al.*[5]. A typical procedure for the preparation of the ester is given below.

Biphenyl-4-p-n-butoxy benzoate.—*p-n*-Butoxybenzoic acid (3·88 g) was refluxed for 3 hours with thionyl chloride (12 ml) using a drop of pyridine. Excess of thionyl chloride was removed under reduced pressure. 4-Hydroxy biphenyl (3·4 g) in dry pyridine (60 ml) was added in one lot to the crude acid chloride, the mixture stirred for 3 hours at room temperature and left overnight. The reaction mixture was poured onto a stirred mixture of concentrated hydrochloric acid and crushed ice, when the ester precipitated out. It was filtered, washed with 10% sodium hydroxide solution, water and dried. Yield, 6·55 g.

The crude ester was chromatographed on neutral alumina (NCl, Poona, Brockmann activity 1) and was eluted with benzene. Removal of the solvent from the eluate afforded a white material, which was crystallized from benzene-light petroleum, m.p. 158–159° C.

ν_{max} 1720, 1605, 1580, 1510, 1170, 980 and 760 cm^{-1}. δ, 1·0 (S, 3 H, $-CH_3$); 1·2 2·0 (*m*, 4 H); 4·18 (*t*, 2 H, $-OCH_2$); 7·0 (*d*, J=8 Hz, 2 H); 7·2, 7·6 (*m*, 9 H); 8·2 (*d*, J=8 Hz, 2 H).

The authors thank Professor S. Chandrasekhar and Dr. N. V. Madhusudana, for helpful discussions. They are grateful to the Department of Organic Chemistry, Indian Institute of Science, Bangalore, for facilities where part of this work was done and to Dr. T. R. Govindachari, Director, CIBA Research Centre, Bombay, for elemental analyses.

Raman Research Institute, Bangalore 560006, *January* 2, 1975.

B. K. SADASHIVA.
G. S. R. SUBBA RAO.*

* Permanent address : Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012.

1. Gray, G. W., Jones, B. and Marson, F., *J. Chem. Soc.*, 1957, p. 393.
2. Dewar, M. J. S. and Schroeder, J. P., *J. Org. Chem.*, 1965, 30, 2296.
3. Bryan, R. F., *J. Chem. Soc.*, 1960, p. 2517.
4. Gray, G. W., Hartley, J. B., Ibbotson, A. and Jones, B., *Ibid.*, 1955, p. 4359.
5. Lauer, W. M., Sanders, P. A., Leekley, R. M. and Ungnade, H. E., *J. Am. Chem. Soc.*, 1939, 61, 3050.

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF COPPER

WE have developed a simple and quick method of determining copper which is based on the reduction of cupric salts with stannous chloride, removal of the excess of the stannous chloride by reaction with mercuric chloride and then oxidising the cuprous salt back to cupric salt with ferric sulphate which results in the production of an equivalent quantity of ferrous sulphate which is then titrated against a standard solution of potassium dichromate. The method is thus very similar to the well-known stannous chloride reduction method of the determination of iron, the major difference being that an inert atmosphere has to be maintained during the time of the removal of the excess stannous chloride with mercuric chloride and till the addition of the ferric sulphate, to prevent the oxidation of the cuprous salt by air which is very much faster than the oxidation of ferrous salts.

Very good results have been obtained by following the procedure described below.

To 10 ml of a solution containing between 0·0100 to 0·1000 g of copper taken in 250 ml conical flask add 10 ml concentrated hydrochloric acid, mix well and then add stannous chloride solution (15 gram $SnCl_2$, 2 H_2O dissolved in 100 ml 6 N HCl) drop by drop till the solution becomes colourless and 2 or 3 drops in excess. Add 1 to 1·5 g sodium bicarbonate followed immediately by 5 ml of a saturated solution of mercuric chloride. Close the flask with an air-tight slopper as soon as the evolution of carbon dioxide stops. Shake gently and wait for 5 minutes for the oxidation of the excess $SnCl_2$ by $HgCl_2$ to go to completion. Remove the stopper and immediately add about 0·5 g sodium bicarbonate followed at once by 20 ml of an approximately N/10 ferric sulphate solution. No air should enter the flask till after the addition of the ferric sulphate solution. Shake and add 3 ml of phosphoric acid and 3 to 4 drops of (0·3%) barium diphenylamine sulphonate indicator solution, dilute to 150 ml and titrate against standard potassium dichromate solution (N/20 or N/10). Each ml of N/10 potassium dichromate is equivalent to 0·006354 g of copper.

Some of the typical results obtained are given in Table I.

TABLE I

Sl. No.	Copper taken (in grams)	Copper found (in grams)	% error
1	0·0944	0·0937	−0·7
2	0·0629	0·0623	−1·0
3	0·0472	0·0470	−0·2
4	0·0315	0·0318	+1·0
5	0·0252	0·0246	−2·5
6	0·0189	0·0183	−3·0
7	0·0157	0·0152	−3·0

The accuracy of the method depends on the efficiency with which air is excluded from the flask during the crucial stages as indicated above.

Only the substances which interfere in the determination of iron by the stannous chloride reduction method (Au, Pt, V, MO, W, Sb, As) interfere in this method of copper determination, besides iron. If interfering substances are present a preliminary separation of copper from them will have to be made in accordance with the classical procedures.

Chemical Laboratory, Geol. Survey of India, Hyderabad 500004, *September* 6, 1974.

C. R. VISWANADHAM.*
V RUKMINI.**
C. NARASIMHA MURTHY.

* Present address : Mineral Exploration Corporation Ltd., Chemical Laboratory, New Secretariat Building, Nagpur.
** Present address : Chemistry Department, Andhra University, Waltair.

EFFECT OF PROTONATION ON THE RESTRICTED ROTATION ABOUT THE EXOCYCLIC C-N BOND OF NUCLEIC ACID BASES

THE stereochemistry and electronic structure of nucleic acid bases have been subjected to intense investigations in the literature[1,2]. The exocyclic C–N bond in these nucleic acid bases possess considerable double bond character[3]. Molecular orbital calculations have been successfully employed to estimate