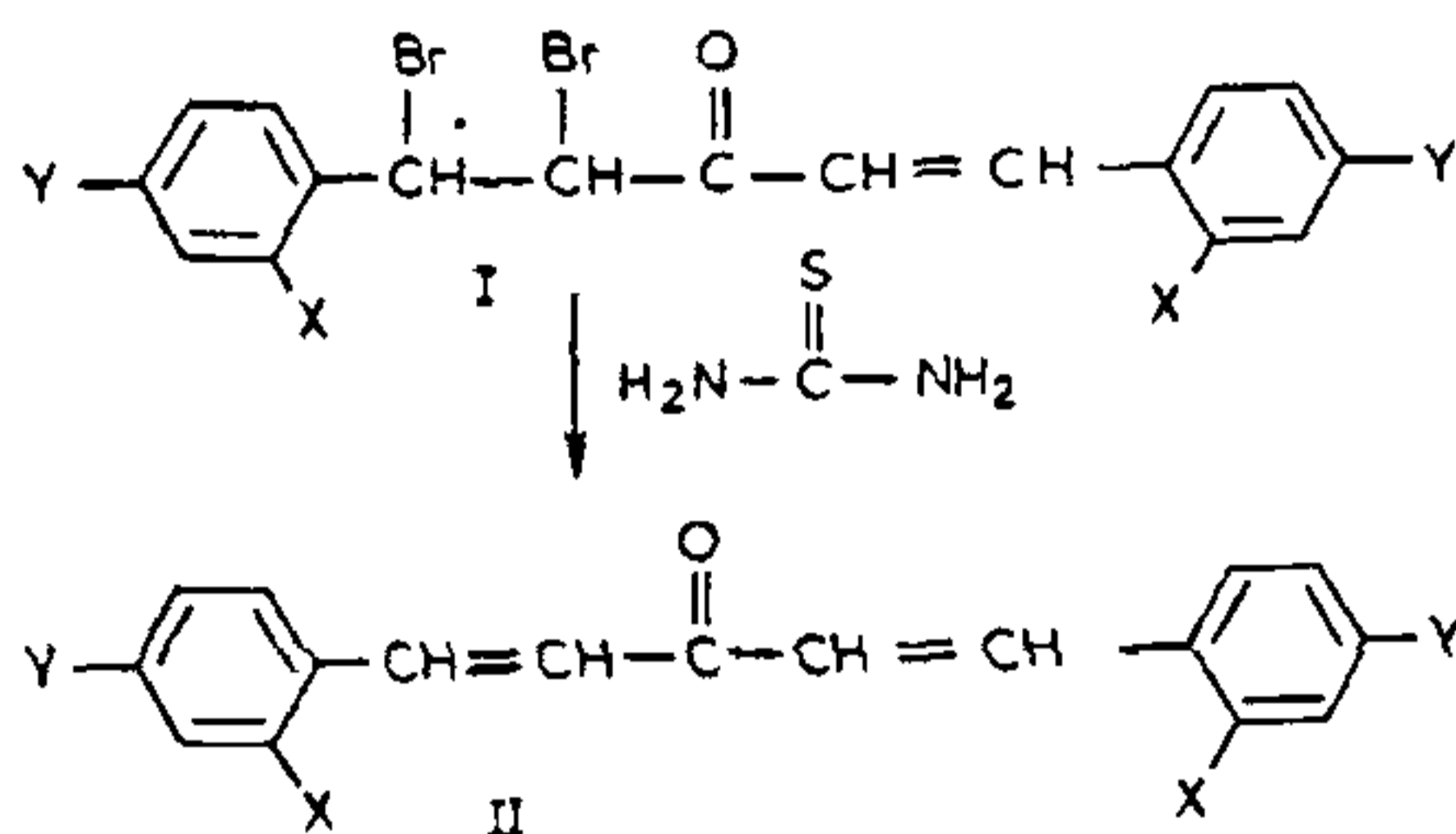


DEBROMINATION OF DIBENZALACETONE DIBROMIDES WITH THIOUREA*

We wish to report that thiourea in ethanol is an effective debrominating agent for dibenzalacetone dibromides under reflux conditions. The impetus for the present study came from the recent report by Sharma and Bokadia¹ that chalcone dibromides on refluxing with thiourea in ethanol suffered debromination yielding chalcones and free sulphur.

We have studied the reaction of six dibenzalacetone dibromides (Ia-f) with thiourea in ethanol under reflux conditions. It is observed that debromination occurs in all the cases yielding dibenzalacetones (IIa-f) and free sulphur. Interestingly, *p,p'*-dimethoxydibenzalacetone dibromide (Ic) underwent debromination spontaneously on exposure to air for about 3 hr, even in the absence of thiourea.

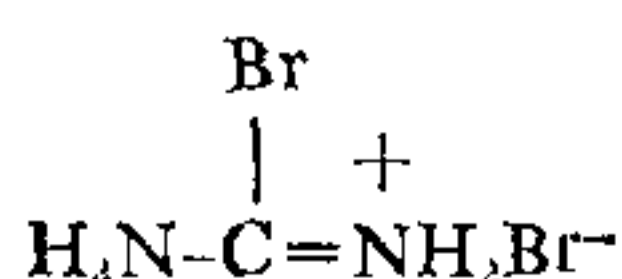


I and II: (a) X = Y = H, (b) X = H, Y = CH₃, (c) X = H, Y = OCH₃, (d) X = H, Y = (CH₃)₂N, (e) X = OH, Y = H, (f) X = Cl, Y = H.

The speculative mechanism proposed by Sharma and Bokadia involving initial nucleophilic attack by thiourea on the α -ketocarbon appears plausible in these cases also.

In a typical experiment, dibenzalacetone dibromide (Ia, 7.9 g), thiourea (1.6 g) and ethanol (100 ml) was refluxed on a water-bath for 4 hr, cooled to room temperature and then poured into cold water (400 ml). The yellow solid that separated was filtered and washed with water. Crystallization from ethanol yielded two products. The sparingly soluble compound on recrystallization from benzene gave bright yellow needles of free sulphur (0.65 g, m.p. 118°). The soluble product was extracted with ether and dried with anhydrous Na₂SO₄. Evaporation of ether gave a pale yellow solid which was recrystallized from ethyl acetate and found to be dibenzalacetone (3 g, m.p. 112°).

Regarding the fate of thiourea in this reaction, we felt that it might have been transformed into



and attempted the isolation of this species. Unfortunately, all our attempts in this regard met with failure. It is possible that this species, if formed, is unstable under the conditions employed.

The authors are grateful to Professor Sp. Shanmuganathan for facilities and encouragement.

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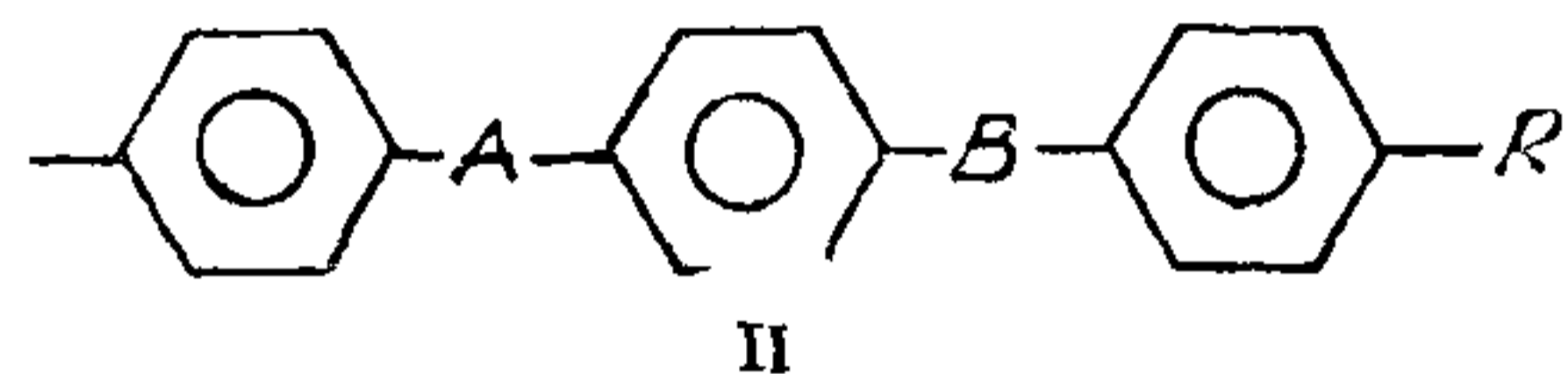
* Formed a part of the thesis accepted for the degree of Master of Philosophy of the University of Madras.

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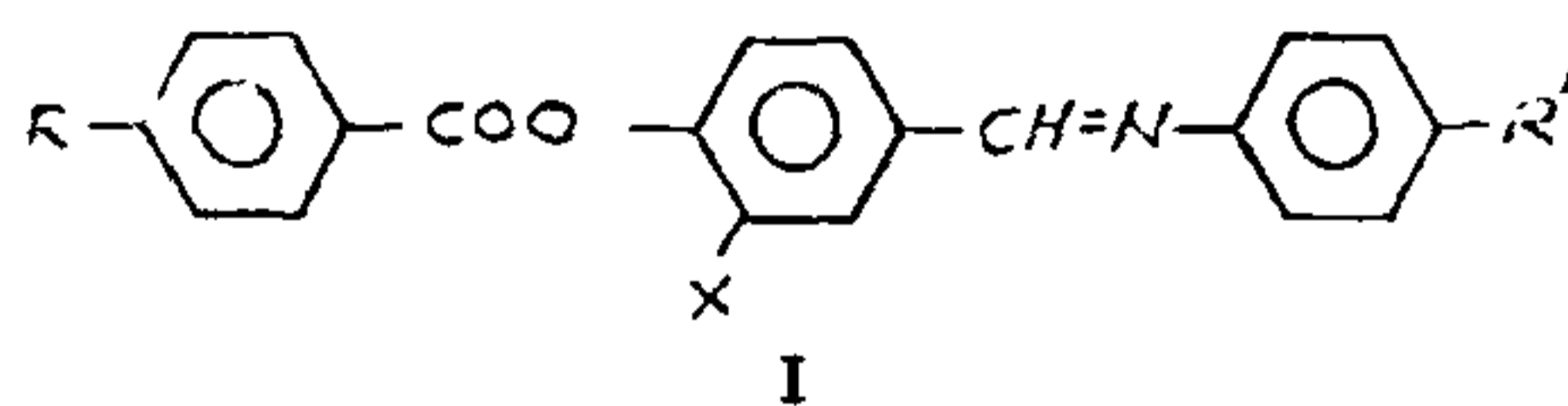
1. Sharma, T. C. and Bokadia, M. M., *Indian J. Chem.*, 1976, 14(B), 65.

EFFECT OF SUBSTITUTION AND ITS LOCATION ON LIQUID CRYSTALLINE PROPERTIES OF PHENYLENE DERIVATIVES*

In quest of new mesogenic materials recently number of systems of the type II is reported where A and B are either ester linkage or azomethine linkage^{1, 2}.



The effect of different substituents is studied on such systems and general observations are deduced about the additivity of different groups. In the present study, we report nine phenylene derivatives having different end and lateral substituents of the type I having unsymmetrical linkage.



Title compounds I were synthesized by condensing *p*-substituted benzoyl chlorides with appropriate aldehydes, *i.e.*, *p*-hydroxy benzaldehyde and vanillin (4-hydroxy-3-methoxybenzaldehyde) using pyridine as condensing agent. The resultant substituted benzoyloxy benzaldehydes were condensed with respective amine by refluxing in alcohol. The Schiff bases crystallized from alcohol till constant transition temperatures were obtained. The analytical data of all the compounds were satisfactory. The melting points and transition temperatures are reported in Table I.

TABLE I

No.	R=	R'	X	Transition temperatures °C	
				Nematic	Isotropic
Ia	CH ₃ O	CH ₃	H	129.0	274.5 ³
Ib	CH ₃	OCH ₃	H	135.0	280.0
Ic	CH ₃	Cl	H	170.0	259.0
Id	CH ₃	CH ₃	H	170.0	240.0
Ie	CH ₃ O	OCH ₃	H	153.5	305.0 ³
If	CH ₃ O	CH ₃	OCH ₃	(155.0)	185.0
Ig	H ₃ CO	OCH ₃	OCH ₃	186.0	204.5
Ih	H ₃ CO	Cl	OCH ₃	(150.0)	170.0
Ii	H ₃ CO	Cl	H	138.0	292.0

The reference to Table I shows that isomeric compounds Ia and Ib have nematic thermal stability difference of 5.5° C which may be due to the unsymmetrical linkage present in the molecules of I.

When two -CH₃ groups (Id) are replaced by two -OCH₃ groups (Ie) in the system I, the nematic-isotropic thermal stabilities increase by 65° C. Now in the case of Ie and Ia, the -OCH₃ group from aniline moiety is replaced by -CH₃ group, the difference in nematic thermal stabilities is 30.5° C. If we consider the additivity of two such groups, the difference in the resultant compound should be of 61° C. Practically we have observed the difference to be 65° C. However, if we consider the replacement of -OCH₃ group in (Ie) by -CH₃ group on the ester side (Ib) the difference of nematic thermal stabilities is of 25° C and if we consider the additivity of two such groups, it should be 50° C. This value is quite low compared to 65° C difference observed when two methyl groups are replaced by two methoxy groups in the system I. These observations clearly indicate that as the molecule is unsymmetrical and the exchanging groups have different polarity, the additivity in thermal stability is not observed in all the cases.

Introduction of lateral substituent like -OCH₃ group in (Ia) decreases the nematic thermal stability by 119.5° C and the mesophase is rendered metastable (If) whereas, in the case of (Ie) introduction of the same -OCH₃ lateral substituent decreases the stability by 100° C and the mesophase is enantiotropic in nature (Ig). In the case of compound (Ii) the introduction of lateral -OCH₃ group renders nematic mesophase metastable and thermal stabilities are decreased by 142° C (Ih).

These results suggest, even though the compounds have the same skeleton (type I) but having different end groups, the introduction of the same lateral substituent -OCH₃ does not have same deterring effect. The decrease in thermal stabilities depend on the overall polarizability of the parent compound and the nature of the end groups.

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1. Van Meter, J. P. and Klanderemann, B. H., *Mol. Cryst. Liq. Cryst.*, 1973, 22, 285.
2. Cole, H. S. and Sowa, J. R., *Ibid.*, 1975, 30, 149.
3. Kurian, G., *Ph.D. Thesis*, M.S. University of Baroda, Baroda, 1976.

HABIT MODIFICATION CAUSED BY CHLORIDE IONS DURING THE ELECTRODEPOSITION OF SILVER FROM CYANIDE BATH ON SILVER (111) FACE

THE morphology of silver electrodeposits deposited on silver single crystals from argento cyanide bath has been studied by several workers to obtain brighter deposits¹⁻⁴. The effects of phosphates, sulfates, chlorides and hydroxides have also been studied⁵ on polycrystalline surfaces. However, very little work on the influence of chloride ions on the morphology of deposits grown on a flat single crystal substrate has been reported. The present experimental work was carried out to study the habit modification of silver electrodeposit, deposited on a silver (111) face from silver cyanide bath in presence of chloride ions.

The electropolishing was carried out as suggested by Shuttleworth, King and Chalmers⁶. The deposition was carried out at 2 mA/cm² and 5 mA/cm² on the (111) face from a solution containing 33.5 g of AgCN and 35 g of KCN and 38 g of K₂CO₃ in a litre of distilled water⁷, to a thickness of 3.6 μ at 24 ± 2. A known amount of A.R. KCl solution was added whenever necessary. Fresh solutions were used for each experiment. The over-potential was measured with reference to a freshly prepared silver electrode using digital pH meter with an accuracy of ± 5 mV. The surface appearance was examined under phase