vary from 102° to 119°. Hydrogen bonds are not yet clear. At this stage, the molecule looks very much twisted along the centre of symmetry. Molecular packing is mainly due to van der Waals forces. Further refinement of the structure is in progress and the details will appear elsewhere.

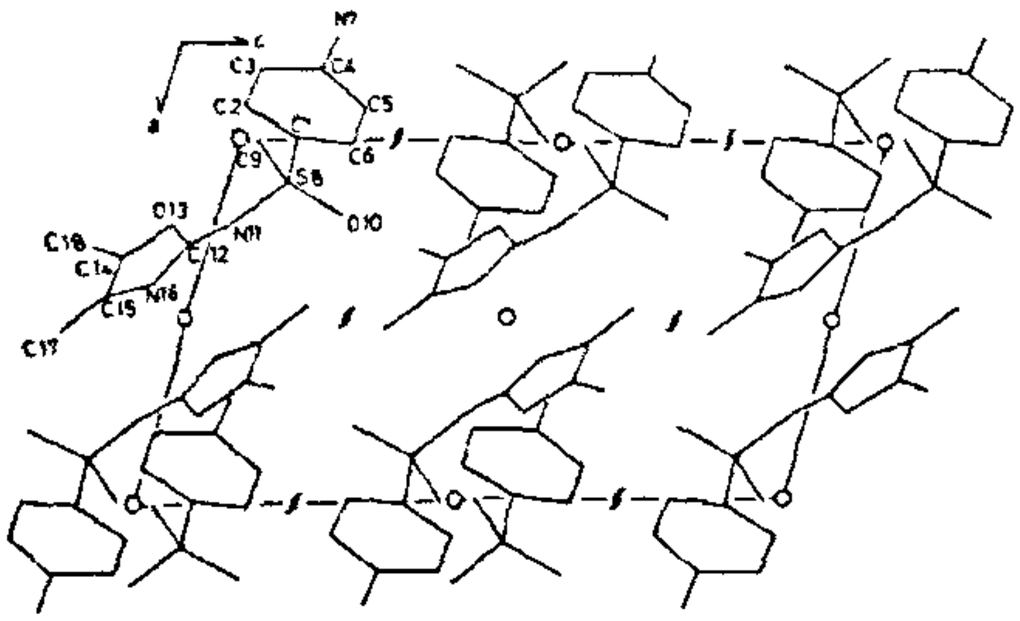

Figure 1. The structure viewed along the *b*-axis.

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1 July 1982

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ACTIVATED NITRILES IN HETEROCYCLIC SYNTHESIS: A NOVEL SYNTHESIS OF PYRIDINONES, QUINOLINES AND THIAZOLINONES

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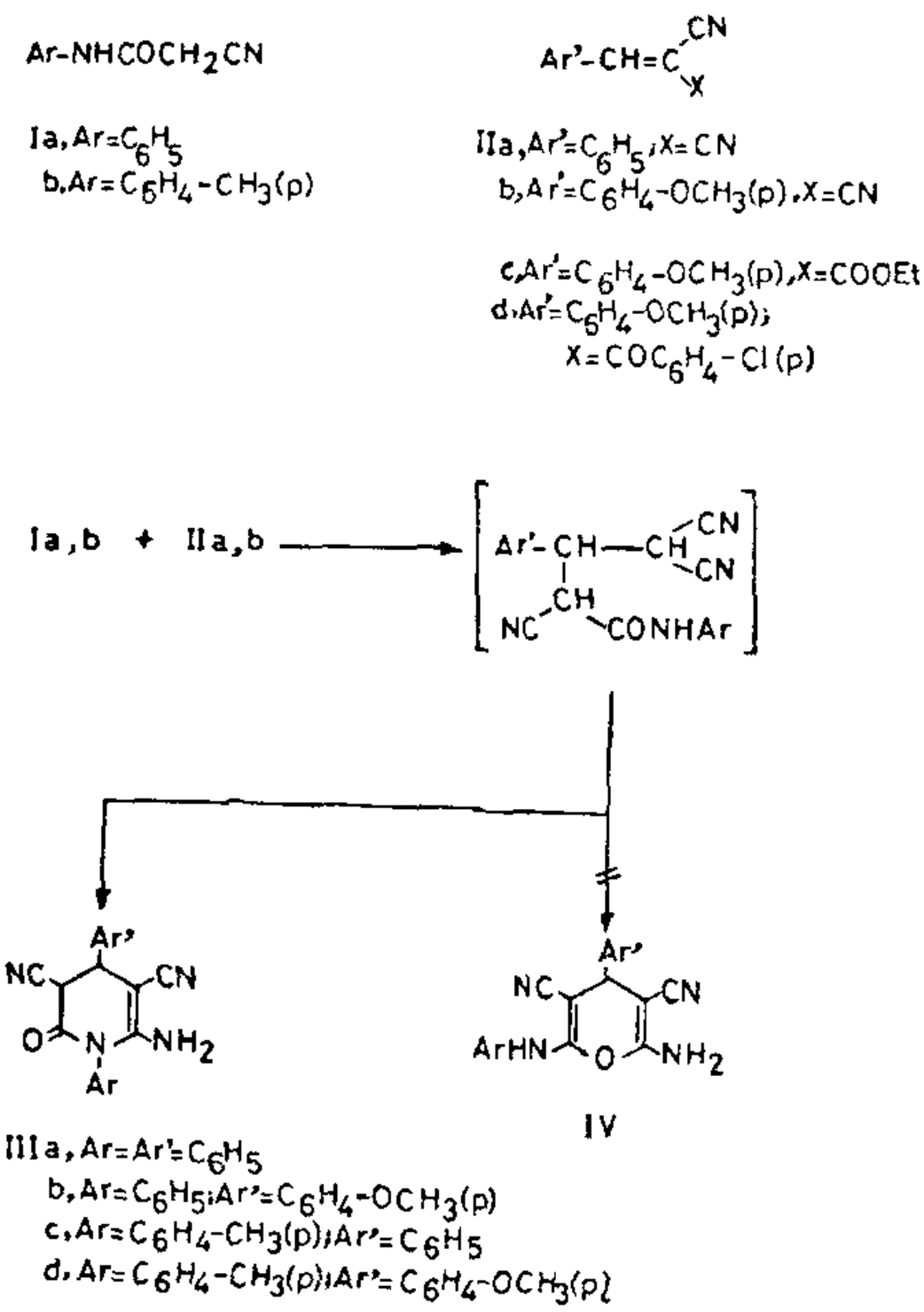
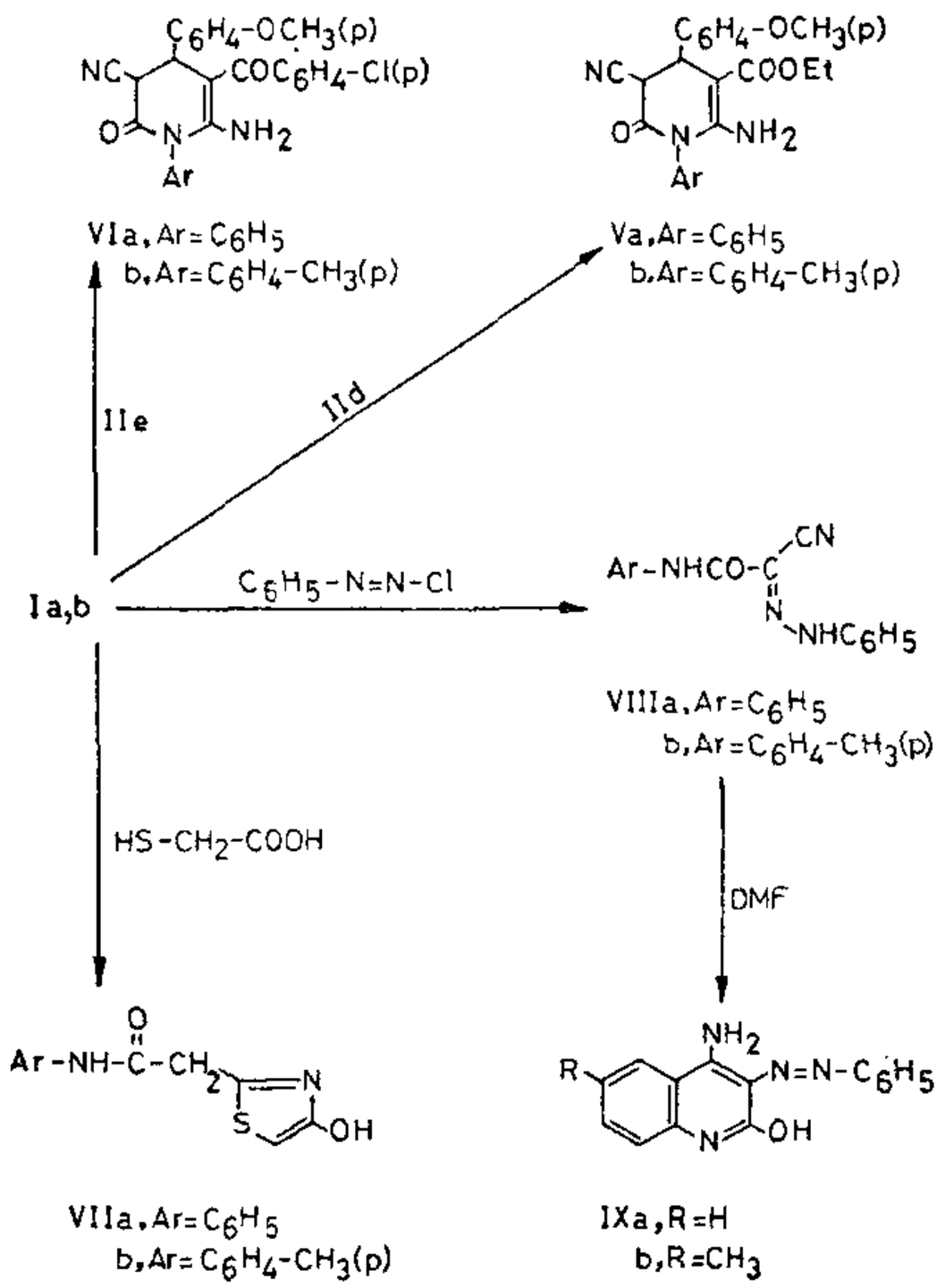
POLYFUNCTIONAL nitriles are versatile reagents extensively utilized in heterocyclic syntheses[1-3]. In continuation of our programme of developing new procedures to synthesise azoles and azines utilizing readily accessible polyfunctional nitriles as starting materials, we report here the utility of cyanoacetanilide (I) for the synthesis of pyridinones, thiazolines and quinolines. It has been found that Ia,b reacted with the cinnamonitrile derivatives IIa,b to yield 1:1 adducts IIIa-d. The IR spectra of the products revealed absorption band characteristic for carbonyl group and another band for amino group. Two theoretically possible isomeric structures were considered (cf. III and IV). However, structure III could be established for the reaction products based on their stability *towards acetic-ammonium acetate mixture. The for*mation of III from the reaction of I and IIa,b is assumed to proceed *via* addition to the activated double bond followed by cyclization of the Michael adduct intermediates.



Similarly, Ia,b reacted with IIc,d under the same conditions to yield the pyridinones derivatives Va,b and Va,b (or alternate tautomers) respectively. A novel synthesis of thiazole was earlier reported *via* reaction of malononitrile, benzalacetonitrile and ethyl cyanoacetate with thioglycollic acid[4-6]. It has now been found that Ia,b reacts with thioglycollic acid to yield 2-carboxamidomethyl-4-hydroxythiazole derivatives VIIa,b.

Compound Ia,b could also be converted into quinolines *via* treatment of their arylazo derivatives with hydrazines or dimethylformamide. This constitutes an interesting direct synthesis of arylazoquinolines IXa,b.



All melting points are uncorrected; IR spectra (KBr) were recorded on a Perkin-Elmer model 21 spectrophotometer. Both the elemental analysis and IR spectra were carried out in the microanalytical unit at Cairo University.

A general procedure for pyridones IIIa-d, Va-b and VIa, b:

A solution of each of Ia and Ib (0.1 mol) in ethanol (100 ml) is treated with each of IIa–e (0.1 mol) then with triethylamine (1 ml). The reaction is heated under reflux for 4 hr and evaporated in vacuo, the residue is then triturated with water and the resulting solid product is collected by filtration and crystallised from a suitable solvent and identified as IIIa,b; Va,b and VIa,b respectively (cf. table 1).

2-(N-Arylacetamido)-4-hydroxythiazolines VIIa, b:

A solution each of Ia and Ib (0.1 mol) in glacial acetic acid was treated with thioglycollic acid (0.01 mol). The reaction mixture was heated under reflux for 4 hr and allowed to cool and poured in water. The solid product so formed was collected by filtration and crystallised from a suitable solvent and identified as VIIa,b (cf. table 1).

TABLE 1

Compounds Synthesised

Compound*	M.P. °C	Yield	Mol. Form.	IR (cm^{-1})
IIIa+	300	60	$C_{19}H_{14}N_4O$	2220 (CN), 1680 (CO)
IIIb+	295	65	$C_{20}H_{16}N_4O_2$	2220 (CN), 1680 (CO), 3300 (NH_2)
IIIc+	318	78	$C_{20}H_{16}N_4O$	2220 (CN), 1760 (CO)
IIId+	310	63	$C_{21}H_{18}N_4O_2$	2220 (CN), 3300 (NH_2), 1680 (CO)
Va′	170	75	$C_{22}H_{21}N_3O_4$	2220 (CN), 1650 (ester CO), 1680 (ring CO)
Vb′	142	71	$C_{23}H_{23}N_3O_4$	2200 (CN), 1650 ester CO), 1680 (ring CO)
VIa′	165	70	$C_{26}H_{20}N_3O_3Cl$	2220 (CN), 3320 (NH_2), 1650 (benzoyl CO), 1680 (ring CO)
VIb′	203	68	$C_{27}H_{22}N_3O_3Cl$	2200 (CN), 3320 (NH_2), 1650 (CO), 1680 (ring CO)
VIIa+	275	76	$C_{11}H_{10}N_2O_2S$	3300 (OH), 1720 (Amide CO)
VIIb+	240	73	$C_{12}H_{12}N_2O_2S$	3300 (OH), 1720 (amide CO)
IXa′	178	60	$C_{15}H_{12}N_4O$	3130 (NH_2), 3500 (OH)
IXb′	192	62	$C_{16}H_{14}N_4O$	3150 (NH_2), 3500 (OH)

*The structures of these compounds were inferred from correct elemental analysis and spectral evidence.

+The solvent for crystallisation was acetic acid.

′The solvent for crystallisation was ethanol.

4-Amino-2-hydroxy-3-phenylazo-6-substituted-quinolines IXa,b:

To a solution of each of VIIIa and VIIIb (0.1 mol) in hydrazine hydrate or phenylhydrazine or dimethylformamide (20 ml) was heated under reflux for 4 hr and allowed to cool and poured into water. The solid product so formed was collected by filtration and crystallised from a suitable solvent and identified as IXa,b (cf. table I).

24 May 1982

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ELECTRON SPIN RESONANCE SPECTROSCOPIC EVIDENCE FOR STERIC ENHANCEMENT OF RESONANCE

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THE phenomenon of steric enhancement of resonance was reported earlier[1] during studies on the dipole moments of some substituted anisoles. Kinetic studies of several trisubstituted benzenes (I) provided additional evidence to support this view[2-5]. Recently, UV spectroscopic evidence also has been reported[6]. In this paper ESR spectral data on radical anions (II) obtained by the electrolytic reduction[7] of the aromatic nitro compounds in acetonitrile are used to substantiate the above phenomenon.

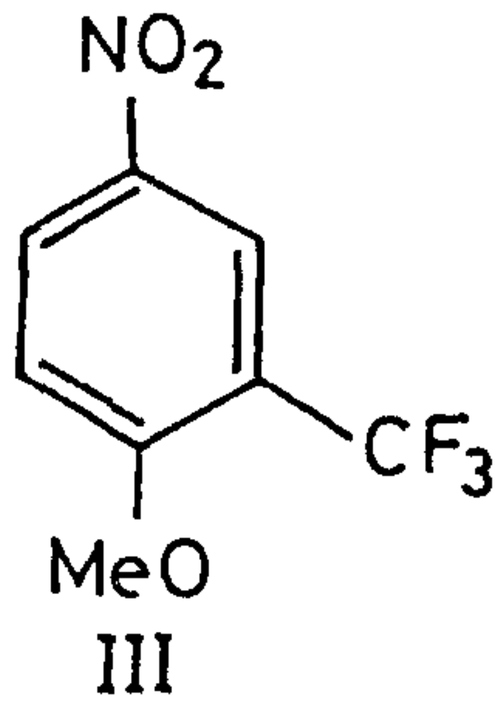
X = Me, Cl, Br, I
Y = COOEt, $COCH_3$, NMe_2, $SOCH_3$

I

Ar = Phenyl or substituted phenyl

II

The ESR spectra of II have been used to study the effect of substituents[7,10]. Geske and Maki[7,8] found that electron withdrawing substituents decrease the hyperfine coupling constant a_N and electron releasing substituents increase it. It was also found that a_N could be related to Hammett function and a plot of



III

TABLE I

Hyperfine coupling constants for nitrobenzene radical anions

Substituents	Hyperfine coupling constant *a* in Gauss: Observed	Calculated
None	10.3[a]	—
2-Methyl	11.0[b]	—
3-Methyl	10.8[b]	—
4-Methyl	10.4[b]	—
2-Trifluoromethyl	8.32[b]	—
3-Trifluoromethyl	8.84[d]	—
4-Methoxy	11.6[b]	—
3-Nitro	4.70[b]	—
2,6-Dimethyl	11.7[c]	11.7
3,5-Dimethyl	10.5[c]	10.6
3,4-Dimethyl	10.9[c]	10.9
2,4,6-Trimethyl	17.8[c]	17.8
2,4,6-Trimethyl-3-nitro	8.20[c]	8.20
2-Trifluoromethyl-4-methoxy	9.20[d]	9.20
3-Trifluoromethyl-4-methoxy	10.9[d]	9.90

Data taken from reference [a] 7; [b] 8; [c] 9; [d] 10.