**238.** *The S_N Mechanism in Aromatic Compounds. Part XXX.[1]*
The Sydnone Ring.

By Chan Tin-Lok, J. Miller, and (in part) F. Stansfield.

The characteristics of the sydnone ring system have been investigated by making kinetic measurements with some 1-chloro-2-nitro-4-X-benzenes (including X = the sydnone ring), and comparing these results with measurements on a suitable series of multiple-bond nitrogen groups.

A close similarity to β-azoxy-grouping is demonstrated and discussed. The Hammett substituent constant (σ^*) for the *p-N*-sydnone ring is 0·710, compared with 0·769 for the *p*-β-azoxyphenyl group. Close similarity to the azido- (or α-azoxyphenyl) group is not supported.

THE sydnones,[2-4] the best known of the meso-ionic compounds, which were reviewed in 1957,[5] are regarded generally as having a positive charge delocalised by aromatic-type 6-π-electron resonance over the whole ring, plus an additional unshared pair on negative oxygen, which, being but little delocalised, causes the carbon–oxygen bond to have little carbonyl character. Baker and Ollis [5] represent *N*-phenylsydnone, for example, as (I)
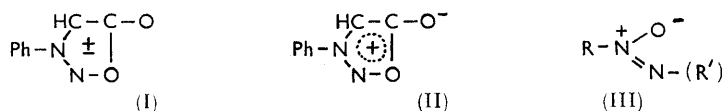
and (II), but favour (II). There is a formal resemblance [5] to the tropone system, though the latter is not included among meso-ionic compounds. Molecular-orbital calculations of this system [6-8] give calculated bond orders (IV) and net charges (V,[6] VI [8]) which Coulson [4] has scaled down, as on (VII), to correspond to the correct dipole moment. While there is numerical divergence in net charges assigned, their relative values and the bond orders are consistent, and the positive charge is then localised mainly on the nitrogen in position 1.
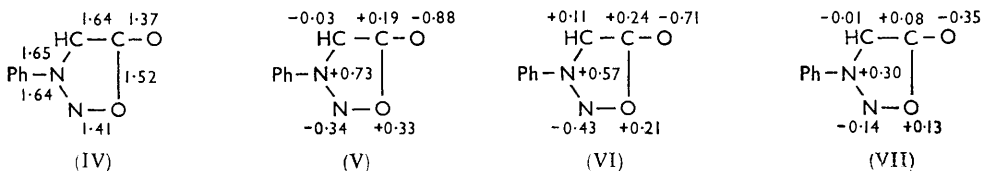
It seems to us that the β-azoxy structure (III) strongly resembles the sydnone system, particularly bearing in mind that there is internal conjugation in the azoxy-group (see below); we thought, therefore, that a suitable extension of Miller and Parker's work,[9] which dealt with a number of multiple-bond nitrogen substituents including azido and α- and β-azoxyphenyl groups, should give important information about the sydnone system.

EXPERIMENTAL

Materials.—*o*-Chloronitrobenzene and 1-chloro-2,4-dinitrobenzene were the purified commercial products.

[1] Part XXIX, Miller and Wan Kai-Yan, *J.*, 1963, 3492.
[2] Earl and Mackney, *J.*, 1935, 899, and subsequent papers.
[3] Baker and Ollis, *Nature*, 1946, **158**, 703.
[4] Coulson, " Valence," 2nd edn., Oxford University Press, London, 1961, pp. 386—388.
[5] Baker and Ollis, *Quart. Rev.*, 1957, **11**, 15.
[6] Hill, Sutton, and Longuet-Higgins, *J. Chim. phys.*, 1949, **46**, 244.
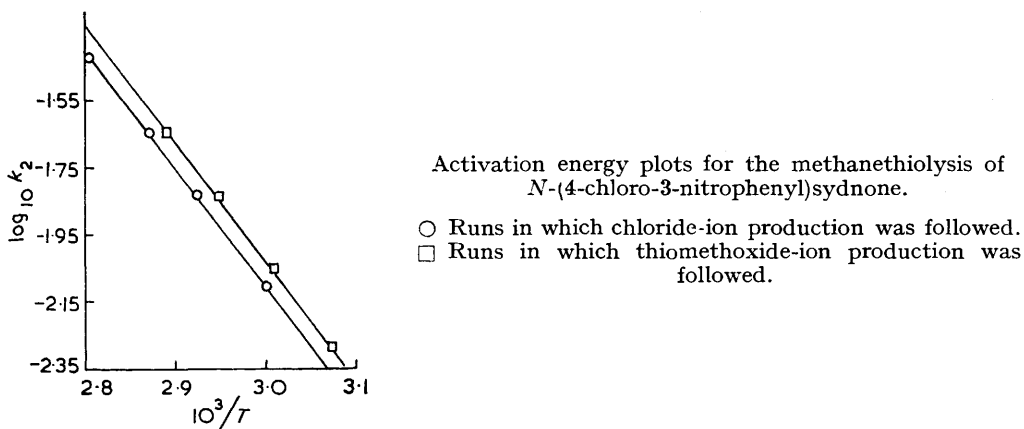[7] Longuet-Higgins, *J. Chim. phys.*, 1949, **46**, 246.
[8] Orgel, Cottrell, Dick, and Sutton, *Trans. Faraday Soc.*, 1951, **47**, 113.
[9] Miller and Parker, *Austral. J. Chem.*, 1958, **11**, 302.

4-*Chloro-3-nitroaniline.* This was prepared by procedures based on that of Morgan and Potter [10] (cf. ref. 11). Yields were variable and our best, below $-4°$, was 80%.

N-(4-*Chloro-3-nitrophenyl)glycine.* An aqueous solution of chloroacetic acid (7·56 g.) was neutralised with N-sodium hydroxide (80 ml.) and added dropwise during 4 hr. to a boiling mixture of 4-chloro-3-nitroaniline (13·8 g.) and water (1 l.) under reflux. Heating was continued for 48 hr., and the clear liquor was decanted from a small amount of brown solid, cooled, finally in the refrigerator, filtered, extracted twice by boiling with ammonia (100 ml., d 0·880, and 500 ml. water in all), and separated from unchanged amine (2 g.; m. p. 99—102°). The filtrate was neutralised, while hot, with concentrated hydrochloric acid, and enough boiling water was added to give a clear (brownish-yellow) solution. On cooling the solution, finally in the refrigerator, the product crystallised as yellow needles (9 g.), m. p. *ca.* 170°, pure enough for subsequent use. A sample recrystallised from propan-2-ol, then from water, gave N-(4-*chloro-3-nitrophenyl)glycine* as long yellow needles, m. p. 177—178° (decomp.) (Found: C, 41·95; H, 3·0; Cl, 15·2. $C_8H_7ClN_2O_4$ requires C, 41·7; H, 3·0; Cl, 15·4%).

N-(4-*Chloro-3-nitrophenyl)-*N-*nitrosoglycine.* A suspension of the crude glycine (2·3 g.), powdered thoroughly, in water (30 ml.) was stirred mechanically and cooled in ice while a solution of sodium nitrite (0·69 g.) in water (20 ml.) was added dropwise during 30 min. 5N-Hydrochloric acid (10 ml.) was then similarly added during 30 min., and the stirring and cooling were continued for a further 30 min. The product was filtered off, washed with water, and air dried; it was a yellow solid (2·43 g.), m. p. 124° (decomp.), and was suitable for the final stage. A sample, recrystallised from 95% alcohol held below 40°, yielded N-(*chloro-3-nitrophenyl)-*N-*nitrosoglycine* as pale yellow needles, m. p. 125—126° (decomp.) (Found: C, 37·0; H, 2·4; Cl, 13·4. $C_8H_6ClN_3O_5$ requires C, 37·0; H, 2·3; Cl, 13·7%).

Activation energy plots for the methanethiolysis of N-(4-chloro-3-nitrophenyl)sydnone.

○ Runs in which chloride-ion production was followed.
□ Runs in which thiomethoxide-ion production was followed.

N-(4-*Chloro-3-nitrophenyl)sydnone.* The crude nitroso-compound (5·5 g.) was dissolved in acetic anhydride (20 ml.). It was allowed to stand for 14 days at room temperature, during which time pale yellow crystals separated. After cooling in the refrigerator, these were filtered off, washed with a little alcohol, and dried. The *product* (1·25 g.) was recrystallised twice from boiling ethanol (in which it is but little soluble), to give pale yellow plates, m. p. 175—176° (decomp.) (Found: C, 40·0; H, 1·6. $C_8H_4ClN_3N_4$ requires C, 39·8; H, 1·65%).

Products. Known (2-nitrophenyl)thioanisole and 2,4-dinitrothioanisole were isolated direct from the corresponding reaction mixtures. N-(4-*Methylthio-3-nitrophenyl)sydnone* was obtained similarly, as a yellow solid (m. p. 190—193°) which was obtained as pale yellow needles, m. p. 196—197° (decomp.) (Found: C, 42·95; H, 3·1; S, 12·7. $C_9H_7N_3O_4S$ requires C, 42·7; H, 3·8; S, 12·65%).

Kinetic Procedure.—Solid sodium thiomethoxide was prepared by Plieninger's method, [12] involving reaction of methanethiol with sodium methoxide, and addition of toluene; it was dissolved in methanol as required for runs. Runs were carried out with equimolar concentrations of the aromatic chloro-compound and sodium thiomethoxide in absolute methanol.

[10] Morgan and Potter, *J.*, 1915, **107**, 652.
[11] Borsche and Exss, *Ber.*, 1923, **56**, 2353.
[12] Plieninger, *Chem. Ber.*, 1950, **83**, 266.

Rate constants (k_2) were obtained by graphical plots, normally after estimating chloride potentiometrically in samples quenched in excess dilute chloride-free nitric acid. The procedure of van Meurs [13] for estimating thiomethoxide was also used for a further four runs with the sydnone. The method as applied here involves quenching of the methanolic reaction mixture in acetone containing aqueous ammonia and titrating with silver nitrate in propan-2-ol, while bubbling nitrogen. Thus, slow reactions presumably occur during titration, with possibly some decomposition of the sydnone ring also. The rate constants thus determined were rather high, as expected, but the values of the Arrhenius parameters were almost identical with those obtained from estimation of chloride (see Figure); the latter data are probably the more reliable. Kinetic and derived data are given in the Table.

Rate constants, and some parameters, for the reaction of sodium thiomethoxide in methanol with some 1-chloro-2-nitro-4-X-benzenes.*

X	$10^4 k_2$ (l. mole⁻¹ sec.⁻¹) (Temp. in parentheses)					Calc. at 0°	$E_{act.}$ (kcal.)	$\log_{10} B$	$S_{act.}$ (e.u.)	S.R.F.† and Hammett substituent constant (σ *) at 0°	
H	‡ 3·24 (85·4)	6·76 (96·0)	11·8 (104·5)	18·8 (111·2)	31·6 (120·0)	0·000986	18·4	$7·7_5$	−24·88	1	0
As(II)	‡ 76·0 (60·0)	142 (68·5)	220 (75·0)	396 (84·2)		0·353	16·2	$8·4_5$	−22·03	3·58 × 10²	0·710
	§ 50·7 (52·5)	85·1 (59·0)	138 (65·4)	219 (72·8)		0·432	$16·0_5$	8·5	−21·80	4·39 × 10²	0·734
NO₂	‡ 36·6 (0·0)	74·8 (7·4)	130 (14·0)	283 (24·5)	323 (25·0)	36·6	14·1	$8·8_5$	−19·85	3·71 × 10⁴	1·270

* Hammett reaction constant (ρ) = 3·60 at 0°.   † Substituent rate factor (Miller, *J.*, 1952, 3550).   ‡ Measured by following production of chloride ion.   § Measured by following disappearance of thiomethoxide ion.

DISCUSSION

Miller and Parker [9] discussed the multiple-bond nitrogen groups in relation to the ability of such groups to withdraw electrons and to facilitate S_N reactions by stabilising a cyclo-hexadienide type of transition state.[14-17] They commented also on the effect of internal conjugation involving O^- (azoxy-groups) and N^- (azido-groups) on this activation. The sydnones resemble vinylogues of β-azoxy-compounds, where the conjugation of the O^- is small; some conjugation of the unshared electrons on the formally neutral ring-oxygen is likely to be similar in extent. The calculations already referred to [6-8] are consistent with this.

Miller and Parker [9] investigated the methanolysis of the chlorine in some 1-chloro-2-nitro-4-X-benzenes, using, among others, *o*-chloronitrobenzene and 1-chloro-2,4-dinitro-benzene to determine a Hammett reaction constant (ρ),[18-20] and thus to obtain values of substituent constants (σ*). Because of the alkali-sensitivity of the sydnone ring itself, which is required intact, we have chosen the more nucleophilic,[21] but less basic, thiomethoxide ion, and measured the rates of methanethiolysis of these two compounds and *N*-4-chloro-3-nitrophenylsydnone (Table and Figure). We find the ρ value at 0° to be 3·60, compared with 4·59 for the methanolysis. The values are comparable, while the smaller value for the methanethiolysis is appropriate for a more powerful reagent. This gives a σ* value for the *p*-*N*-sydnone ring = 0·710 (0·734 from runs estimating SMe⁻), compared with 0·595 and 0·769 for the *p*-α- and *p*-β-azoxyphenyl groups, and 0·083 for

[13] van Meurs, *J. Electroanalyt. Chem.*, 1961, **2**, 17.
[14] Miller, *Revs. Pure Appl. Chem. (Australia)*, 1951, **1**, 171.
[15] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.
[16] Bolto and Miller, *Austral. J. Chem.*, 1956, **9**, 74 and 304.
[17] Daly, Kruger, and Miller, *Austral. J. Chem.*, 1958, **11**, 290.
[18] Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96; *Trans. Faraday Soc.*, 1938, **34**, 156.
[19] Jaffé, *Chem. Rev.*, 1953, **53**, 191.
[20] Miller, *Austral. J. Chem.*, 1956, **9**, 61.
[21] Miller, *J. Amer. Chem. Soc.*, 1963, **85**, 1628.

View Online

1216   *The S_N Mechanism in Aromatic Compounds.   Part XXX.*

the *p*-azido-group.   It is thus very similar to, but slightly less activating than, the β-azoxy-group.

The values of $E_{act.}$, $\log_{10} B$, and $S_{act.}$ also confirm the β-azoxy-analogy.   In methanolysis of the 1-chloro-2-nitro-4-X-benzenes the 4-nitro-group reduces $E_{act.}$ by 6·2 kcal. and the β-azoxyphenyl group by $4·1_5$ kcal.   In the methanethiolysis the 4-nitro-group reduces $E_{act.}$ by 4·3 kcal., so that the corresponding reduction for *p*-β-azoxyphenyl is 2·9 kcal. The reduction observed for the *p*-N-sydnone ring is 2·2 ($2·3_5$ from runs estimating SMe$^-$); only a little less activating.   It is not really worth discussing at length the relative values of $\log_{10} B$ and $S_{act.}$, since the differences are not much bigger than experimental error.   It is noteworthy, however, that they are all low, and this seems a characteristic of the larger nucleophiles;[21] the sydnone values, like the β-azoxyphenyl values are intermediate between the mono- and di-nitro-compounds.

The effect of the β-azoxy-group, though modified a little by internal conjugation, is regarded[9] as due both to the nitrogen attached to the benzene ring bearing positive charge, and a double bond (=N) conjugated with the ring.   This is supported by the near absence of activation by the azido-group, in which we regard the ring-attached nitrogen as bearing a fractional negative charge and the bond to its neighbouring nitrogen as having relatively low bond-order.[9]   We would not agree, therefore, that the azido-group, or the aliphatic diazo-group, is a close analogue of the sydnone system,[22] but now draw a close analogy with the β-azoxy-group.   This implies not only a substantial localisation of positive charge on the 1-nitrogen, as Baker and Ollis[5] have suggested, but also that there may be little delocalisation energy in the sydnone ring system over and above an amount similar in magnitude and origin to that within an azoxy-group.   Thus, the resemblance to the tropones[5] may not extend to a comparable degree of aromaticity. Our views are also well supported by the low reactivity of the benzene ring in *N*-phenyl-sydnone towards S_E reactions,[5] since the azido-, azophenyl, and α-azoxyphenyl groups, attached by nitrogen with available unshared electrons, are among the groups which activate both S_E and S_N reactions,[9,20,23,24] whereas the β-azoxy-group does not activate the ring attached to the N$^+$–O$^-$ of the azoxy-group,[23,25] and thus resembles the sydnones. Also, azoxy-groups are *N*-analogues of the nitro-group.   In the latter, both N–O bonds are of the same order, intermediate between single and double bonds, whereas the lack of symmetry in the azoxy-groups, and different electronegativities of nitrogen and oxygen, would lead to a higher bond-order for the N–N than for the N–O bonds.   Thus structure (III) more nearly resembles the true structure of the β-azoxy-group than does the corresponding formal structure to that of the nitro-group.

The character of thiomethoxide ion as a nucleophilic reagent has been referred to by Miller[21] and investigated more fully by Miller and Wong,[26] and is therefore not discussed further here.

(C. T.-L., J. M.) UNIVERSITY OF HONG KONG, HONG KONG.
(F. S.) UNIVERSITY OF KHARTOUM, SUDAN, E. AFRICA.   [*Received, June 24th,* 1963.] ·

[22] Baker, Ollis, and Poole, *J.,* 1949, 307.
[23] Hassan, Karamalla, and Miller, unpublished work.
[24] Robertson, Hitchings, and Will, *J.,* 1950, 808; Robertson, de la Mare, and Swedlund, *J.,* 1953, 782.
[25] " Chemistry of Carbon Compounds," ed. Rodd, Vol. IIIA, Elsevier, London, 1954, p. 315.
[26] Miller and Wong, unpublished work.