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POLAROGRAPHY OF NON-BENZENOID AROMATIC AND RELATED SUBSTANCES—VI*

POLAROGRAPHIC AND SPECTROPHOTOMETRIC STUDY OF STERIC HINDRANCE OF COPLANARITY IN 3-PHENYLSYDNONES

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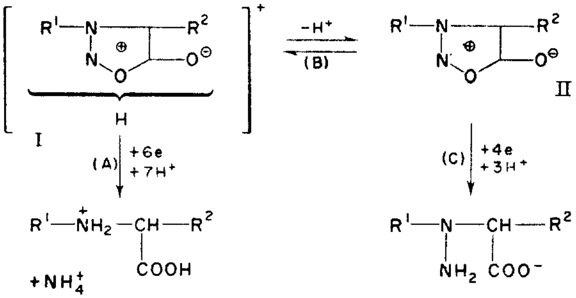
Abstract—Substitution of alkyl groups on the *ortho*-position of 3-phenylsydnone causes a steric hindrance in coplanarity of the sydnone and phenyl rings. This was proved from the shift of the polarographic half-wave potentials (in excess of the polar effects), from the ultra-violet spectra, and from scale models. The behaviour of 3-*o*-tolylsydnone resembles more that of 3-benzylsydnone than that of 3-phenylsydnone. In 3′,4′-dihydroquinolino[1′,2′-*c*]-sydnone, the —CH_2 CH_2— bridge brings the sydnone and phenyl rings into a nearly coplanar position, shown on scale models, and its polarographic and spectrophotometric behaviour resembles that of 3-phenylsydnone.

EVIDENCE given in previous parts of the series[1–4] has shown that the sydnones are a class of organic substances very suitable for following the effects of constitution on polarographic curves. On the other hand, it was possible to show that polarography enables us to measure in a simple manner parameters, permitting one to distinguish and measure the influence of polar and mesomeric effects of substituents.

The reduction of sydnones at the dropping mercury electrode proceeds according to the following scheme:‡



Due to restoration of the equilibrium (B) in the neighbourhood of the dropping mercury electrode, the six-electron reduction waves of the protonated form (I) are

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* Part V: *Coll. Czech. Chem. Comm.* in press.

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‡ We use here formula recommended by W. Baker[5], as officially adopted by the Chemical Society (London), although we have reservations regarding the suitability of this formula for best expressing all the physical and chemical evidence.

[1] P. Zuman *Coll. Czech. Chem. Comm.* **25**, 3245 (1960).

[2] P. Zuman *Coll. Czech. Chem. Comm.* **25**, 3252 (1960).

[3] P. Zuman *Coll. Czech. Chem. Comm.* **25**, 3265 (1960).

[4] P. Zuman *Coll. Czech. Chem. Comm.* in the press.

[5] W. Baker *Proc. Chem. Soc.* 76 (1959).

observed even at pH ca. 5, even when the equilibrium concentration of form I under such conditions is extremely low. The four-electron waves corresponding to (C), observed at pH above 7, are pH-independent. Their half-wave potentials are best suited for the study of effects of substituents R^1 and R^2. Using such values we were able to show[3] that *meta-* and *para*-substituents on the phenyl rings in 3-phenyl- and 3,4-diphenylsydnones follow the modified Hammett equations.[6,7] Thus such substituents exert primarily polar effects. For sydnones in which R^1 and R^2 were different alkyl, aryl, and other groups, we were able[4] to prove the validity of the modified Taft equation.[6–8] Based on $E_{1/2}$-σ^* plots we could distinguish† that whereas the phenyl group on C-(4) exerts only a polar effect, the phenyl group on N-(3) shows both a polar effect and a resonance interaction with the sydnone ring.

On the other hand, up to the present there is little evidence in the literature for the effects of substituents on the ultra-violet spectra of sydnones. The spectra of six sydnones, of quite diverse types, were published by Earl *et al.*[9] These showed that the general shape of the spectrum of 3-phenylsydnone was not greatly altered in 3-*p*-bromophenylsydnone and 4-bromo-3-phenylsydnone, although the extinction coefficients are enhanced.

The spectra of three of the aforementioned sydnones (phenyl-, benzyl- and diphenylsydnones) were published by Baker *et al.*,[10] as well as that of 3-cyclohexylsydnone. These authors pointed out that as this last is a true alkylsydnone, and as interannular conjugation in 3-benzylsydnone is prevented by the methylene group, the band at 292 mμ which both exhibit must be due to the sydnone ring. A conjugation shift in 3-phenylsydnone was pointed out, as well as the appearance of a small extra band at 238 mμ, identified as arising from a shift in the ethylenic absorption of the benzene ring. The much greater displacement of the sydnone band (to 333 mμ) in 3,4-diphenylsydnone was explained as being due to the extra conjugation arising from the presence of a third aromatic ring.

The published spectrum of 4-bromo-3-phenylsydnone shows somewhat less conjugation than the parent compound, or the isomeric *p*-bromophenylsydnone, but in the present paper we restrict ourselves to the discussion of the effects of alkyl groups in the *ortho* and C-(4) positions in 3-phenylsydnone, and some effects of ring formation on polarographic half-wave potentials and ultra-violet spectra.

EXPERIMENTAL

Substances. 3-Phenylsydnone and 4-methyl-3-phenylsydnone was kindly presented by J. C. Earl (Thurlton, England), 3-*o*-methoxy- and 3-*o*-ethyoxyphenylsydnone by R. A. Eade (School of Applied Chemistry, Sydney) and 3-*o*-methoxy- and 3-*p*-methoxyphenylsydnone by Farbenfabrik Bayer A. G. (Leverkusen). 3-Methyl-, 3-*m*-tolyl-, 3-*o*-tolyl-, 3-*o*-ethylphenyl-, 4-methyl-3-*o*-tolyl, 4-methyl-3-*p*-tolyl, 4-methyl-3-(2′,6′-xylyl)-, tetrahydropyrido[*c*]-, and 3′,4′-dihydroquinolino[1′,2′-*c*]sydnones were prepared by the methods of Hammick *et al.*[11,12]

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† Assuming that the value of $\sigma^*_{C_6H_5} = 0{,}60$ given by Taft[8] is a quantitative measure of the polar effect only.

[6] P. Zuman *Coll. Czech. Chem. Comm.* **25**, 3225 (1960).

[7] P. Zuman: *Ricerca Sci.* **30**, (1960).

[8] R. W. Taft, Jr., *Separation of Polar, Steric and Resonance Effects in Reactivity* in M. S. Newman, *Steric Effects in Organic Chemistry.* John Wiley, New York (1956).

[9] J. C. Earl, R. J. W. Le Fèvre and I. R. Wilson, *J. Chem. Soc.* Suppl. 105 (1949).

[10] W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.* 310 (1949).

[11] D. Ll. Hammick, A. M. Roe and D. J. Voaden, *Chem. & Ind.* 251 (1954).

[12] D. Ll. Hammick and D. J. Voaden, to be published.

Polarography. A Heyrovský-type polarographic apparatus was used, employing the usual polarographic circuitry, photographic registration, and a Kalousek vessel with a separated calomel electrode. The galvanometer had a sensitivity of 2·4 × 10^{-9} amp/mm. The dropping electrode, used in most experiments, had the following constants: m = 2·3 mg/sec; t_1 = 3·7 sec at h = 63 cm.

Stock solutions (0·0025 M) of the substances mentioned were prepared by dissolving the crystalline products in 50% aqueous ethanol. Buffer solutions were prepared from reagent grade chemicals. The final concentration of ethanol in solutions submitted to polarographic electrolysis was 1%.

It was proved that the dependence of half-wave potentials on pH has a form similar to that of other alkyl and aryl sydnones.[1] It was thus sufficient to measure the half-wave potentials in the alkaline region only. Borate buffer pH 9·2 and 0·17 M NaOH were chosen as suitable supporting electrolytes.

The following technique was adopted for the measurement of half-wave potentials: 9·8 ml of the supporting electrolyte were de-aerated in the Kalousek vessel for about 1 min, 0·2 ml of the 0·0025 M stock solution of the sydnone added, and nitrogen introduced for a further 30 sec. The curve was registered with a low potential span (50–100 mV/absc) with slow scanning. Curves were recorded both from positive to negative potentials, and in the opposite direction. On the same polarogram, curves for a 5 × 10^{-5} M Tl^+ solution were registered. The half-wave potentials were measured and the average values (from curves registered in both directions) computed.

The half-wave potentials were calculated relatively to that of thallium(I) (−0·445 V.vs. S.C.E.) and expressed against the S.C.E. Half-wave potentials determined in this way were reproducible to ±0·003 V.

Spectrophotometry. Determinations of ultra-violet spectra were carried out under the supervision of Dr. F. B. Strauss (Oxford), using a Beckman Model DU Quartz Spectrophotometer. The spectra were measured in solutions in ethanol or methanol, concentrations of the sydnones ranging from 0·5 to 2 × 10^{-5} M.

RESULTS AND DISCUSSION

Polarographic results are summarized in Figs. 1–3 and in Table 1, and the spectrophotometric data in Figs. 4–5.

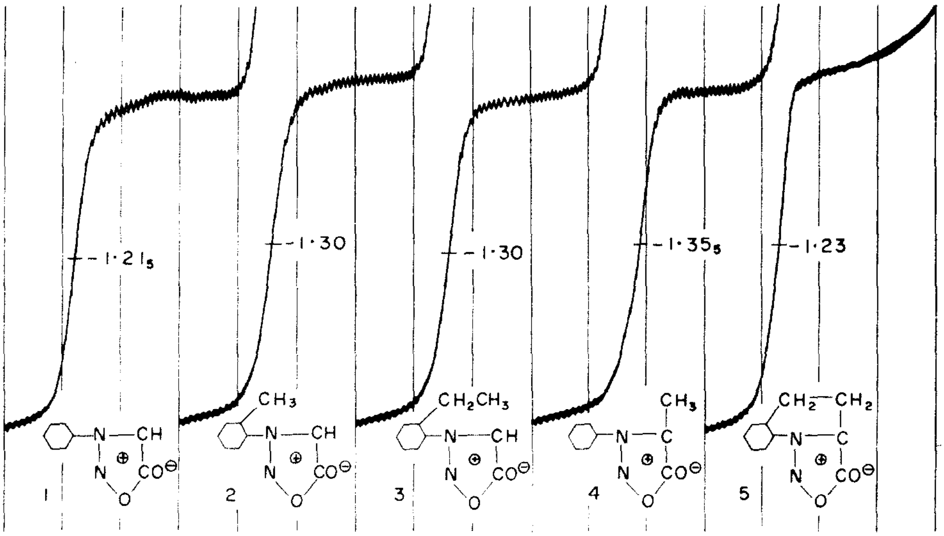

FIG. 1. Polarographic curves of some sterically hindered sydnones
5 × 10^{-5} M Sydnone in 0·17 M NaOH. (1) 3-Phenylsydnone; (2) 3-*o*-tolylsydnone; (3) 3-*o*-ethylphenylsydnone; (4) 4-methyl-3-phenylsydnone; (5) 3′,4′-dihydroquinolino[1′,2′-*c*]-sydnone. Curves starting at 0·8 V, S.C.E., 200 mV/absc, h = 65 cm, sens. 1:10.

We shall first discuss the rôle of the effect of alkyl substitution at the *ortho* position of the phenyl ring in 3-phenylsydnone. In both this sydnone and 4-methyl-3-phenylsydnone the substitution of *o*-alkyl groups on the 3-phenyl ring causes a shift of half-wave potentials towards more negative potentials. If this shift were due to the polar

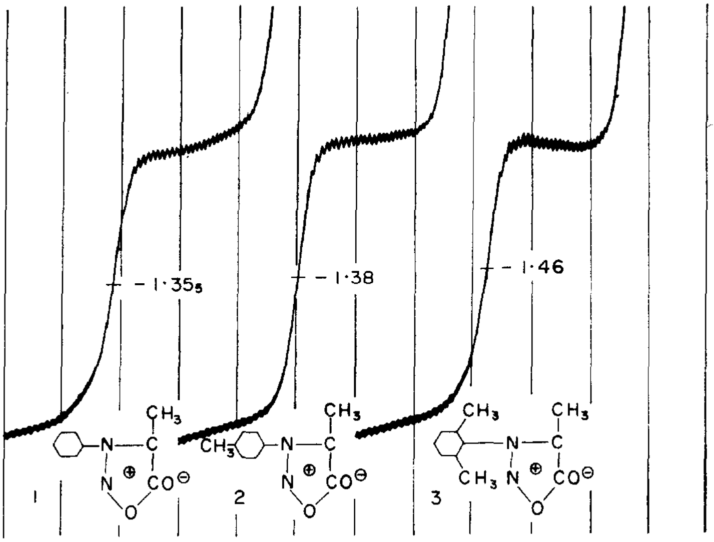

FIG. 2. Polarographic curves of substituted 4-methylsydnones
5 × 10^{-5} M Sydnone in 0·17 M NaOH. (1) 4-Methyl-3-phenylsydnone; (2) 4-methyl-3-*p*-tolylsydnone; (3) 4-methyl-3-(2′,6′-xylyl)-sydnone. Curves starting at 1·0 V, S.C.E., 200 mV/absc, h = 65 cm, sens. 1:10.

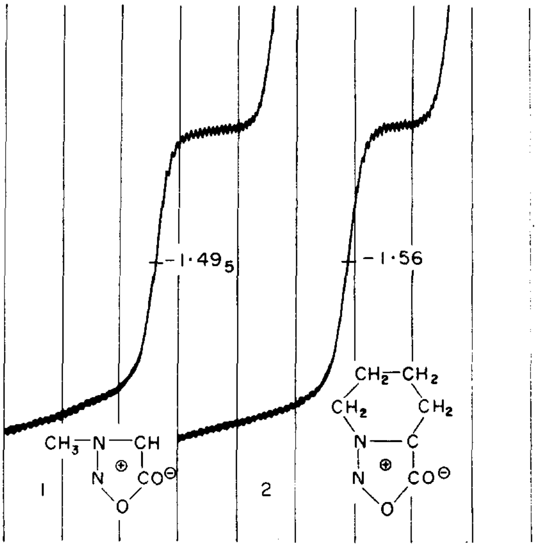

FIG. 3. Effect of ring closure on polarographic curves of sydnones
5 × 10^{-5} M Sydnone in 0·17 M NaOH. (1) 3-Methylsydnone; (2) tetrahydropyrido[*c*]sydnone. Curves starting at 1·0 V, S.C.E., 200 mV/absc, h = 65 cm, sens. 1:10.

effect of the alkyl group only, it would be very approximately of the same order of magnitude as a shift caused by the same substituent in the *para* position.[13] For the case of 3-phenylsydnone, the value of the half-wave potential of 3-*p*-tolylsydnone was not available. As the half-wave potentials of *m*- and *p*-substituted sydnones follow the modified Hammett equation,[3] the value for the shift of half-wave potential caused by a

[13] P. Zuman, Dr. Sc. Thesis, Czechoslovak Academy of Science, Prague (1959).

TABLE 1. HALF-WAVE POTENTIALS OF 5 × 10^{-5} M SYDNONES IN 0·17 M NaOH

	$E_{1/2}$ (V *vs.* SCE)	$\frac{RT}{\alpha nF}$	$(\Delta E_{1/2})_H$[a]
3-Phenylsydnone	−1·21$_5$	0·060	0·00
3-*o*-Tolylsydnone	−1·30	0·061	−0·08$_5$
3-*o*-Ethylphenylsydnone	−1·30	0·060	−0·08$_5$
3-*o*-Methoxyphenylsydnone	−1·26$_5$	0·050	−0·05$_0$
3-*o*-Ethoxyphenylsydnone	−1·25$_5$	0·056	−0·04$_0$
3-*p*-Methoxyphenylsydnone	−1·25$_5$	0·051	−0·04$_0$
4-Methyl-3-phenylsydnone	−1·35$_5$	0·058	0·00
4-Methyl-3-*p*-tolylsydnone	−1·38	0·061	−0·02$_5$
4-Methyl-3-(2′,6′-xylyl)-sydnone	−1·46	0·058	−0·10$_5$
3′,4′-Dihydroquinolino-[1′,2′-*c*]sydnone	−1·23	0′052	—
3-Methylsydnone	−1·49$_5$	0·062	—
3-*n*-Butylsydnone	−1·51	0·065	
Tetrahydropyrido[*c*] sydnone	−1·56	0·060	—
3-Benzylsydnone	−1·42$_5$	0·060	—

[a] Difference of the half-wave potentials of substituted and parent compounds.

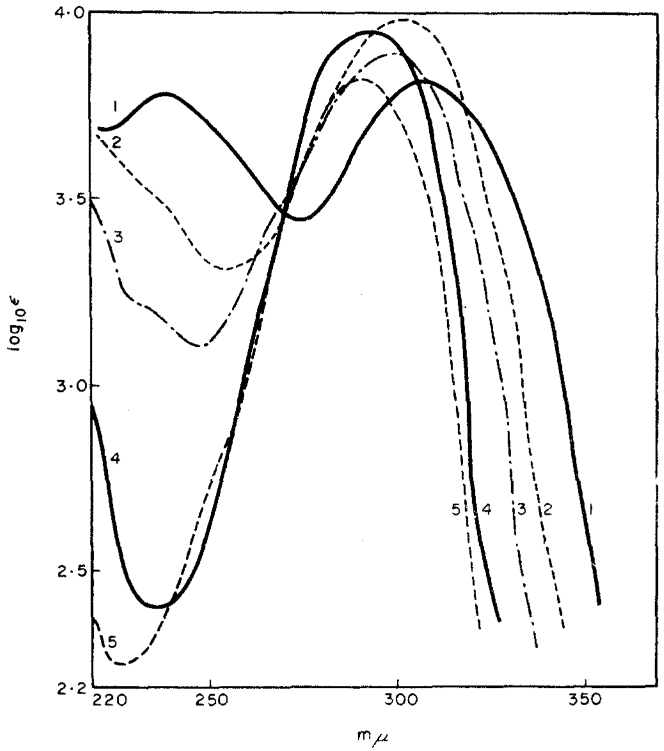

FIG. 4. Absorption spectra of sydnone derivatives
(1) 4-Methyl-3-*p*-tolylsydnone; (2) 4-methyl-3-*o*-tolylsydnone; (3) 4-methyl-3-(2′ 6′-xylyl) sydnone, (4) tetrahydropyrido[*c*]sydnone; (5) 3-methylsydnone.

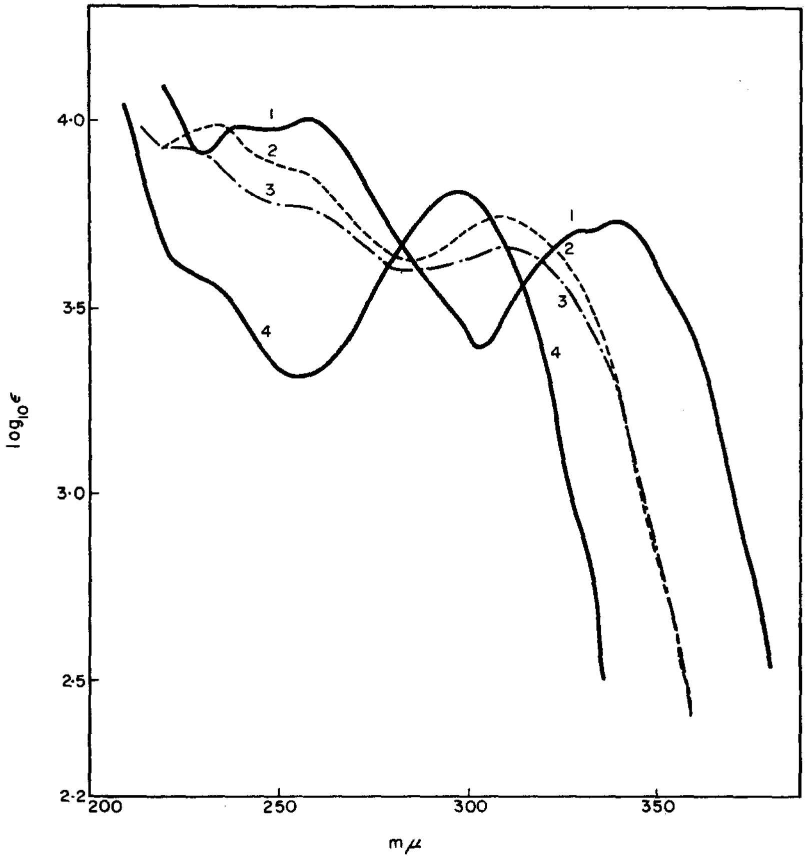

FIG. 5. Absorption spectra of sydnone derivatives
(1) Dihydroquinolino[1′,2′-c]sydnone; (2) 3-phenylsydnone; (3) 3-*m*-tolylsydnone; (4) 3-*o*-tolylsydnone identical with 3-*o*-ethylphenylsydnone.

p-CH_3 group can be computed as $\Delta E_{1/2} = \rho_{\pi,R}\sigma_X = 0{\cdot}18 \times -0{\cdot}17 = -0{\cdot}03$ V. The observed shift ($-0{\cdot}08_5$ V) for 3-*o*-tolyl-sydnone (Table 1) is thus substantially greater than that predicted for the polar effect alone. It is supposed that this excessive influence, causing a more difficult reduction, can be explained by the steric hindrance of co-planarity. In 3-phenylsydnone, besides the polar effect of the phenyl ring on the reducibility of the sydnone, there is a resonance interaction between these two rings.[4] Such an interaction (not detected[4] for the phenyl group in position 4) causes a shift of the half-wave potential to more positive values. If this interaction is at least partly hindered by the bulky *ortho*-substituent, a shift of the half-wave potentials towards more negative values is to be expected, in accordance with the observed value (Table 1). Similar effects of steric hindrance of co-planarity on polarographic half-wave potentials were observed earlier for nitro[14,15] and azo-compounds.[15]

The quantitative measure of the steric hindrance of co-planarity is the difference between the observed shift ($-0{\cdot}08_5$ V) and that computed for the polar effect only

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[14] M. Fields, C. Valle and M. Kane, *J. Amer. Chem. Soc.* **71**, 421 (1949).

[15] Ch. Prevost, P. Souchay and Ch. Malen, *Bull. Soc. Chim. Fr.* **18**, (5), 714 (1951).

(−0·03 V). This difference (−0·05$_5$ V) thus expresses the diminution of resonance interaction between the sydnone and phenyl rings due to the steric effect of the *ortho*-substituent. This value is smaller than the value of −0·10 V deducted for the resonance contribution of the 3-phenyl group obtained[4] from the deviation from the Taft equation (i.e., by a completely different method). This is in agreement with the fact that not all the resonance interaction need be removed by the steric hindrance.

On the other hand, introduction of a methyl-group in position 4 into 3-phenylsydnone exerts only a polar effect on the half-wave potentials. This was proved by the fact that the half-wave potential of 4-methyl-3-phenylsydnone fits well the modified Taft equation for other 4-substituted-3-phenylsydnones.[4] No steric hindrance of co-planarity of the sydnone and 3-phenyl ring could thus be detected for 4-methyl-3-phenylsydnone.

The effects of *ortho* substituents on the phenyl ring in 4-methyl-3-phenylsydnone can be handled as for 3-phenylsydnone. Here the shift due to the *p*-CH_3 is available experimentally from the difference of half-wave potentials of 4-methyl-3-phenylsydnone (−1·35$_5$ V) and 4-methyl-3-*p*-tolylsydnone (−1·38 V). Its value is thus −0·02$_5$ V for one and −0·05 V. for two *o*-methyl groups. The observed shift of −0·10$_5$ V. for the 2,6-xylyl-derivative gives, after subtraction of the polar contribution, the value −0·05$_5$ V. for the shift due to the steric hindrance of resonance, in exact agreement with the value found for 3-phenylsydnone. The effect of the 4-methyl group on the value of the reaction constant $\rho^*_{\pi,\mathrm{R}}$ in the modified Taft equation[4] has not been determined so far, and so an estimation of the resonance contribution from free energy relationships cannot be performed here.

The coincidence of the value of half-wave potentials for 3-*o*-tolylsydnone and 3-*o*-ethylphenylsydnone can be explained by supposing that the relative steric orientation of both rings is about the same in both compounds. The lengthening of the alkyl chain thus does not cause any substantial further distortion. According to the modified Hammett equation[3,6] the polar effects of the methyl and ethyl groups included in the observed shifts cause practically the same increments of the shifts of half-wave potentials in this case. Thus the increment due to the steric hindrance of co-planarity for 3-*o*-ethylderivatives is about the same as that computed for 3-*o*-methyl.

A further argument for the rôle of the steric hindrance of co-planarity is the polarographic behaviour of 3′,4′-dihydroquinolino[1′,2′-*c*]sydnone. This compound shows a substantial shift of the half-wave potential to more positive values in comparison with the values for *ortho* alkyl substituted 3-phenylsydnones. The value of the half-wave potential for this compound with its closed ring is similar to that of 3-phenylsydnone, the difference being of the order of the polar effect of an alkyl group borne by the phenyl ring only. It is thus supposed that in 3′,4′-dihydroquinolino[1′,2′-*c*]sydnone, the relative positions of the sydnone and phenyl rings (permitting the resonance interaction) are closer to the arrangement in 3-phenylsydnone than in 3-*o*-ethylphenylsydnone.

Contrary to the findings with 3-*o*-methyl derivatives no substantial hindrance of co-planarity could be detected for 3-*o*-methoxy- and 3-*o*-ethoxyphenylsydnones. The alkoxy substituents exert practically only a polar effect, as shown by the coincidence of their half-wave potentials with that for 3-*p*-methoxyphenylsydnone (Table 1). This can be explained by flexing of the side chain further away from the 3-phenyl group permitting a preferable configuration without influencing the co-planarity.

The ultra-violet spectra are in complete agreement with these findings. The substitution of a methyl group in the *meta* position, producing 3-*m*-tolylsydnone (Fig. 5), or in the *para* position, as in 4-methyl-3-*p*-tolylsydnone (Fig. 4), influences very little the character of the spectra of the parent compounds lacking these methyl groups. On the other hand, the presence of *ortho*-methyl groups in 3-*o*-tolyl-, 3-*o*-ethylphenyl-, and 4-methyl-3-*o*-tolylsydnones causes a decrease in the extinction of the absorption band at 260 mμ (in 3-phenylsydnones) or 240 mμ (in 4-methyl-3-phenylsydnones). However, the position of the band occurring at the longest wavelength is little affected by substitutions in the phenyl ring.

Paralleling the polarographic findings, the spectroscopic behaviour of 3′,4′-dihydroquinolino[1′,2′-*c*]sydnone resembles much more that of 3-phenylsydnone than that of 3-*o*-alkylphenylsydnones. Thus in this case the spectra offer another proof that the interaction of the phenyl and sydnone rings, lessened by *ortho*-alkyl groups, is restored by ring formation.

Furthermore, in accordance with polarographic findings, the spectra of 3-*o*-tolylsydnone and 3-*o*-ethylphenylsydnone are almost identical (Fig.5).

Another parallel between polarographic curves and spectra is seen when the behaviour of 3-phenyl-, 3-*o*-tolyl-, 3-benzyl, and 3-methylsydnones are compared (Figs. 4 and 5). Polarographic half-wave potentials are shifted towards more negative values in the sequence given. In this same sequence, the extinction coefficients in the range 220–260 mμ also diminish (Figs. 4 and 5). The behaviour of 3-*o*-tolylsydnone both in polarographic and spectral properties lies between that of 3-phenylsydnone and 3-methylsydnone, and closely resembles that of 3-benzylsydnone, where actually only the polar effect of the phenyl group can exert its influence on the sydnone ring.

Comparison of scale models gave further support for the steric hindrance of co-planarity. Using the angles and dimensions indicated by Earl[16] and enlarging them to a scale of 1 cm per Å, wooden models of sydnone rings were made according to the suggestions of Harrell and Corwin.[17] These were then used in conjunction with commercial "Catalin" models.

For 3-phenylsydnone, a flat model (though with the possibility of a twist from co-planarity) can be constructed, as well as for 3′,4′-dihydroquinolino[1′,2′-*c*]sydnone. The flat configuration achieved with the latter model can be taken as a strong indication that the —CH_2CH_2-bridge holds the benzene and sydnone ring in a co-planar configuration.

A model of 3-(2′,6′-xylyl)-4-methylsydnone illustrates well the great twist between the two aromatic rings, the angle between the rings at the point of closest approach being roughly 40°.

It remains to discuss the effect of ring formation in tetrahydropyrido[*c*]sydnone (Fig. 3 and 4). The six-membered ring cannot be assumed to be planar, and thus the Mills-Nixon effect[18] cannot be expected to operate (cf.[19]). In accordance with this assumption, both the ultra-violet spectra and the scale models show that there is little difference between tetrahydropyrido[*c*]sydnone and alkylsydnones.

[16] J. C. Earl, *Chem. & Ind.* 1284 (1953).[17] B. Harrell and A. H. Corvin, *J. Chem. Educ.* **32,** 186 (1955).

[17] B. Harrell, A. H. Corvin, *J. Chem. Ed.* **32,** 186 (1955).

[17a] Recent crystallographic studies by H. Bärnighausen, F. Jellinek and A. Vos [*Proc. Chem. Soc.* 120 (1961)] detected a small twist of 27°, in agreement with our conclusion.

[18] W. H. Mills, I. G. Nixon, *J. Chem. Soc.* 2510 (1930).

[19] P. Zuman, *Chem. Listy* **48,** 94 (1954).

However, polarographic measurements show that whereas the ring formation does not exert any effects of the type derived from steric hindrance of co-planarity, there is some influence from polar and steric strain forces. For this purpose, we shall compare the values for 4-methyl-3-phenylsydnone ($-1{\cdot}35_5$ V) with that for 3′,4′-dihydroquinolino[1′,2′-*c*]sydnone ($-1{\cdot}23$ V). As was shown in a previous paper[4] and mentioned here on p.136 the effect of the 4-methyl group is primarily not an effect on the co-planarity of the phenyl and sydnone rings, but a polar effect of this group. Thus in both compounds compared, the phenyl and sydnone rings being more or less co-planar, the ring formation causes a decrease of the influence of the 4-alkyl group.

A similar comparison can be done for 3,4-diethylsydnone, which should be compared with tetrahydropyrido[*c*]sydnone ($-1{\cdot}56$ V). For the first substance, the value of the half-wave potential is missing, but we can compute it: we shall first derive the value for 3,4-dimethylsydnone. The effect of substituents is principally additive.[6,13] We can thus compute the shift due to a 4-methyl substitution in a sydnone ring, and add this shift to the value for 3-methylsydnone ($-1{\cdot}49_5$ V). The values for $(\Delta E_{1/2})_{4-CH_3}$ are:—

	$E_{1/2}$	$(\Delta E_{1/2})_{4-CH_2}$
3-phenylsydnone	$-1{\cdot}21_5$	
4-methyl-3-phenylsydnone	$-1{\cdot}35_5$	$-0{\cdot}14_0$
3-*o*-tolylsydnone	$-1{\cdot}30$	
4-methyl-3-*o*-tolylsydnone	$-1{\cdot}43_5$[a]	$-0{\cdot}13_5$

[a] From the value for 3-xylyl-4-methylsydnone ($-1{\cdot}46$ V) minus the polar increment for one *o*-CH_3 group ($0{\cdot}02_5$ V).

Thus the mean shift due to a 4-methyl substituent can be taken as $-0{\cdot}14$ V and the calculated value for 3,4-dimethylsydnone is $-1{\cdot}63_5$ V. As both the values of the reaction constants $\rho^*_{\pi,R}$ for 3-substituted sydnones (0·24 V) and for 4-substituted sydnones (0·22 V) are positive and of the same order of magnitude[4] the shift due to the change from 3,4-dimethyl- to 3,4-diethylsydnone is about $2 \times \rho^*_{\pi.R}\sigma^*_{C_2H_5}$, i.e., $2 \times 0{\cdot}23 \times -0{\cdot}1 = 0{\cdot}04$ V. The value of the half-wave potential for the 3,4-diethylsydnone can thus be expected to be about $-1{\cdot}68$ V.

The value ($-1{\cdot}56$ V) found for tetrahydropyrido[*c*]sydnone is thus again more positive than that computed for the corresponding compound with an open ring ($-1{\cdot}68$ V).

The shift ($+0{\cdot}12$ V) due to the ring closure is of about the same order as with the quinoline derivative ($+0{\cdot}12_5$ V).

Whereas the influence on redox potentials of a ring condensed with a quinoid system has already been discussed elsewhere,[19] we know so far of only one example of the comparison of the influence of alkyl substituents on a reducible ring with the effect of a condensed hydrogenated six-membered sing. In quinoxaline and 5,5-benzoquinoxalines[20] substituted at position 2 and 3 with a tetramethylene chain, the ring is reduced at about 0·05 V more positive potential than the corresponding 2,3-dimethyl compound. The direction of the shift due to the polar and steric strain effects involved in the ring formation is thus the same as that observed with sydnones.

[20] R. Curti and S. Locchi, *Ann. Chim.* **45**, 1244 (1955).