

302. Cyclic Meso-ionic Compounds. Part V.* Further Studies on the Stereochemistry of the Sydnones, with a Description of a Heterodyne Capacitance Meter for Dielectric-constant Measurements in the Range 2—3.

By R. A. W. HILL and L. E. SUTTON.

Electric dipole-moment measurements on 4-chloro-3-*p*-chlorophenylsydnone, on 3:4-diphenylsydnone and its *p*-chloro-derivatives (two mono- and one di-substituted), and on the corresponding *p*-tolyl compounds, provide further evidence (cf. Part II, Hill and Sutton, *J.*, 1949, 746) that, in the sydnones, the radial bond from nitrogen lies in the plane of the ring, or very near thereto. Also, closer limits have been found for the angle between this valency and the one which radiates from the neighbouring carbon atom (76—83°), which make it probable that the latter bond also lies in, or nearly in, the plane of the ring.

Both of these stereochemical conclusions support the monocyclic structure with non-localised π -bonds, the so-called meso-ionic structure, which was recently proposed.

We now describe the capacitance meter used for the measurements reported in this and in related papers published since 1947. It is of the heterodyne type; and it gives adequate sensitivity (± 0.0001), combined with ease of operation, for dielectric constants in the range 2—3.

ELECTRIC dipole moments have been used by two groups of workers to investigate the structure of the sydnones (Earl, Leake, and Le Fèvre, *Nature*, 1947, **160**, 366; *J.*, 1948, 2269; Baker, Ollis, Poole, Barltrop, Hill, and Sutton, *Nature*, 1947, **160**, 366; Hill and Sutton, *J.*, 1949, 746; *J. Chim. physique*, 1949, **46**, 244). The principal aim has been to discover whether the dicyclic structure (I) or the recently proposed monocyclic structure (II) is the more correct. The latter can be formulated either as a hybrid of a number of



zwitterionic structures or, following the molecular-orbital procedure, as a structure with partial formal charges (see Baker, Ollis, and Poole, *J.*, 1949, 307; Hill and Sutton, *loc. cit.*); this is represented qualitatively in formula (II).

Two tests have been applied. The first is based on the absolute magnitude of the actual

* Part IV, *J.*, 1951, 289.

moment, which has already been shown to be in substantially better agreement with that expected from (II) than with that from (I). By using new parameters in an empirically corrected molecular-orbital treatment, a revised value has been calculated for the π -electron moment, *viz.*, 5.6 D (Orgel, Cottrell, Dick, and Sutton, *Trans. Faraday Soc.*, 1951, **47**, 113), which agrees quite well with the observed value of 4.6–5.4 D previously reported (Hill and Sutton, *loc. cit.*). In the present paper, an attempt has been made to narrow the limits of the observed value.

The second test is based on the stereochemistry of the system. Were formula (I) correct, the bonds R–N₍₃₎ and R'–C₍₄₎ should not be coplanar with the ring but might be up to 55° out of its plane; whereas if formula (II) were correct, the σ -bonds round C₍₄₎ and N₍₃₎ (which latter has a large positive formal charge) would probably arise from sp^2 hybridisation and be approximately planar, so that the two bonds mentioned would be coplanar with the ring and with each other. This test has not previously given a conclusive answer, although in 3-phenylsydnones the bond Ph–N₍₃₎ has been shown to lie within 20° of the plane of the ring. Further measurements are now reported which bear on this. They also relate to the angle between the valencies radiating from atoms N₍₃₎ and C₍₄₎, and to the angle which μ_π makes with the ring system.

EXPERIMENTAL

Preparation and Purification of Materials.—Benzene. Analytical-grade material was purified as described in Part II (Hill and Sutton, *loc. cit.*).

Sydnones. The sydnones were provided by Professor Wilson Baker and Drs. W. D. Ollis and V. D. Poole (Bristol). Their preparations and characteristics have been reported (*J.*, 1949, 307; 1950, 1542)

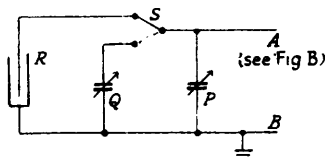
Physical Measurements.—Dielectric constants. A heterodyne-beat capacitance meter was used. This instrument, having proved satisfactory during five years of regular use, is now described in greater detail. It was designed for rapid, routine measurements in the range 2–3.

The principles of measurement are the same as those used earlier (see Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668), *i.e.*, the dielectric constants of air (e_1) and of benzene (e_2) are assumed known, so if e_3 is the value for a solution, and c_1 , c_2 , and c_3 are the corresponding capacities, then

$$e_3 = (e_2 - e_1)(c_3 - c_1)/(c_2 - c_1) + e_1$$

provided that, in the liquid cell, few lines of force pass through more than one medium and that lead capacitances stay constant. The capacitances need be known only in units of an arbitrary linear scale.

FIG. A.



The circuit of the measuring system is shown in Fig. A,* P is an uncalibrated variable capacitor and S is a change-over switch by means of which the calibrated capacitor Q and the cell R may be interchanged; R is connected, and P is adjusted until the difference of frequency from an arbitrary reference frequency, *i.e.*, $\overline{f_1 - f_0}$, is simply related to a fixed audio-frequency f_2 ; then Q is connected and adjusted to give the same result. The process is repeated to compare Q and R accurately, the precision being limited only by the reproducibility of capacitances within the switch S and those for the step units in Q (see later), and by uncontrolled disturbances occurring during the time required to operate S . These factors are made smaller than corresponds to the required precision ($\pm 10^{-4}$), with the result that very rapid and reliable measurements are possible; moreover, changes of dielectric constant with time are easily followed.

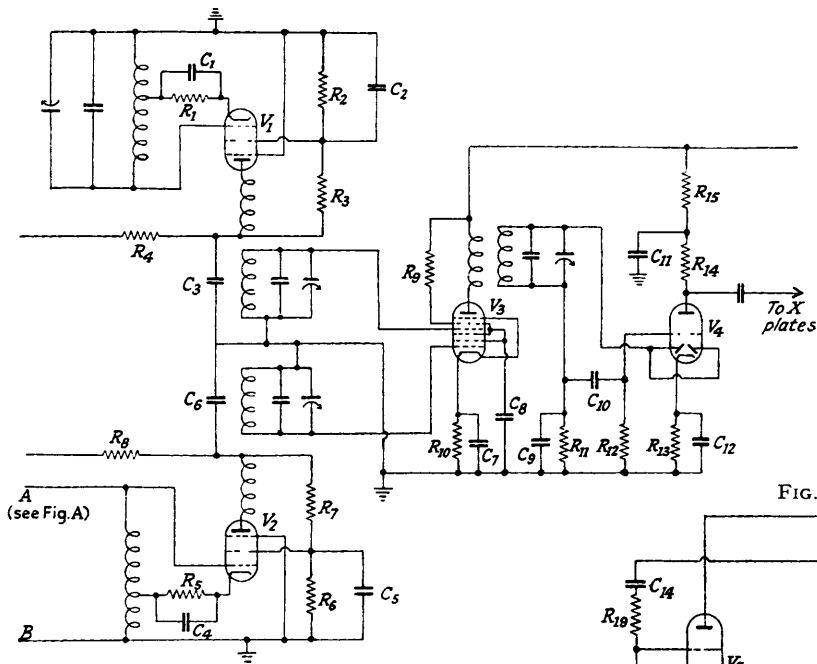
P consists of two capacitors, allowing coarse and fine adjustment; Q consists of the cylindrical capacitor already specified (Sutton, *loc. cit.*) and a set of six silica-insulated capacitors

* Figures in this paper are denoted by letters in order to distinguish them from those of Part II, to which frequent reference is made and which are distinguished numerically as usual.

which can be switched in by keys; R is similar to the cell described by H. O. Jenkins and Sutton (*J.*, 1935, 609) save that the insulated electrode is hollow, and that inside it is a concentric, earthed cylinder forming part of the base assembly; so the electrical capacity is increased to about 50 pF, and the fluid capacity reduced to about 40 ml.* The switch S is a rotary one which gives small and reproducible capacitances between contacts. It consists of a rectangular duralumin plate (2" \times 3") having a spindle through the middle, and at each corner a polystyrene pillar carrying a gold-platinum alloy contact. A polystyrene rod attached to the spindle is slotted axially and across a diameter to carry a silver-plated phosphor-bronze strip which rotates with it and connects together with a wiping action either pair of the diagonally-placed contacts. To give the required operation, two adjacent contacts are connected together.

The apparatus is in three rack-mounted units. The main unit (I), which is essentially a

FIG. B.

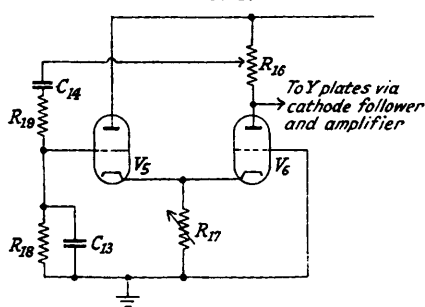


$R_1, R_5 = 5 \text{ k}\Omega$; $R_2, R_6 = 30 \text{ k}\Omega$; $R_3, R_7, R_{14} = 50 \text{ k}\Omega$;
 $R_4, R_8 = 20 \text{ k}\Omega$; $R_9 = 60 \text{ k}\Omega$; $R_{10} = 300 \Omega$; $R_{11} = 500 \text{ k}\Omega$;
 $R_{12} = 1 \text{ meg.}\Omega$; $R_{13} = 1 \text{ k}\Omega$; $R_{15} = 15 \text{ k}\Omega$.

$C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8 = 0.1 \text{ mF.}$; $C_9 = 0.0002 \text{ mF.}$;
 $C_{10} = 0.02 \text{ mF.}$; $C_{11} = 8 \text{ mF.}$; $C_{12} = 50 \text{ mF.}$

$V_1, V_2 = \text{EF } 36$; $V_3 = \text{EK } 32$; $V_4 = \text{EBC } 33$.

FIG. C.



$R_{16} = 100 \text{ k}\Omega$; $R_{17} = 5 \text{ k}\Omega$; $R_{18}, R_{19} = 200 \text{ k}\Omega$.

$C_{13}, C_{14} = 0.001 \text{ mF.}$

$V_5, V_6 = \text{H } 63$.

beat-frequency generator, contains the measuring system and the two radio-frequency oscillators together with subsidiary circuits for mixing, de-modulation, and beat-frequency amplification. The output (frequency $f_1 - f_0$) has an amplitude determined largely by the selectivity of the mixing circuits which are peaked at f_0 . This makes the initial rough tuning very simple. f_0 is approx. 600 kc./sec., which is high enough to give adequate sensitivity but low enough to ensure that the total inductance needed to resonate with the capacitances to be measured is large compared with lead inductances.

The second unit (II) contains an audio-frequency oscillator (f_2 is approx. 1000 cycles/sec.) and a small cathode-ray tube the Y plates of which carry f_2 and the X plates $f_1 - f_0$. The

* A miniature glass cell, used subsequently, is described by Everard and Sutton (*J.*, 1951, 16).

necessary relation between these two frequencies is obtained by tuning to a Lissajous figure : the " figure of eight " corresponding to $\overline{f_1 - f_0} = f_2/2$ is convenient and does not give any loss of sensitivity due to the oscillators " pulling."

Details of the main unit (I) are shown in Fig. B. The oscillators are electron-coupled and the inductive coupling in the plate circuits is made as loose as is compatible with a usable output. Frequency stability is thus improved, and " pulling " is made small. Great care was taken to construct the unit rigidly in order to keep stray capacitances constant. The coils are mounted inside strong brass screening cans in such a way that there would be no relative movement should the main chassis become twisted. The circuits and layouts of the oscillators are as nearly identical as possible, so that disturbances common to both, particularly supply-voltage fluctuations, will have an equal effect on f_0 and f_1 .

The audio-frequency oscillator, the circuit of which is shown in Fig. C, is governed by a Wien bridge. The output is taken through a cathode follower (valve type 6C5) and an amplifier (valve type 6C5)

The power supplies (unit III) are conventional except that there are two high-tension supplies : a regulated supply for the oscillators and cathode follower and an unregulated supply for the other valves. The heaters of the oscillator and cathode follower valves are supplied from a voltage-regulating transformer. The supply for the cathode-ray tube is in unit II.

The linearity of the standard capacitor Q may conveniently be checked by using two Lissajous figures to define a small capacity increment (cf. Groves, *J.*, 1939, 1144); though, as a further check, a calibration was made by the usual method of repeatedly connecting and disconnecting a small fixed capacitance, and was found to agree within the required limits.

The lead from unit I to the cell R , which is immersed in a thermostat (usually at 25°), is taken through a brass tube $\frac{3}{4}$ " in diameter in which it is fixed and insulated with polystyrene discs. Ordinary concentric cable was insufficiently stable.

Specific Volumes.—A pycnometer was used as described in Part II (*loc. cit.*).

Refractive Indices.—Measurements were made with a Jamin interferometer as described in Part II, but these results have since been discarded as unreliable because of a possible dispersion-effect error (Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, 46, 417). Instead, electron polarisations calculated from Earl, Leake, and Le Fèvre's observed value for *N*-phenylsydnone (*loc. cit.*) have been used. The largest discrepancy between the old and the new values is 8.6 c.c., corresponding to a change in moment of 0.03 D. Fortunately, all the moments reported in Part II are negligibly altered (by 0.01 D or less) by the recalculation.

Results.—The observed and derived numerical values are given in Table I, the symbols having the same meaning as in Part II. The procedure for calculating electric dipole moments is also the same (cf. Everard, Hill, and Sutton, *loc. cit.*).

TABLE I.

$w \cdot 10^6$	e	v	$w \cdot 10^6$	e	v	$w \cdot 10^6$	e	v
3 : 4-Diphenylsydnone			4-Phenyl-3-p-tolylsydnone			3 : 4-Di-p-chlorophenylsydnone		
1994	2.3130	1.1441	1153	2.2974	1.1451	334	2.2751	—
3441	2.3415	1.1435	2589	2.3281	1.1444	959	2.2800	—
4895	2.3703	1.1429	2716	2.3306	1.1443	1870	2.2871	1.1445
7300	2.4183	1.1420	4891	2.3765	1.1436	2965	2.2958	1.1438
						3960	2.3038	—
3-Phenyl-4-p-tolylsydnone			4-p-Chlorophenyl-3-phenylsydnone			4975	2.3121	1.1426
1482	2.3018	1.1450	(175)	(2.2764) *	—	7512	(2.3310) †	1.1414
2997	2.3316	1.1446	557	2.2810	—	4-Chloro-3-p-chlorophenylsydnone		
3836	2.3482	1.1443	1096	2.2891	—	1950	2.2940	1.1446
4631	2.3638	1.1441	2123	2.3041	1.1443	3988	2.3175	1.1433
			4796	2.3445	1.1429	6383	2.3455	1.1422
3 : 4-Di-p-tolylsydnone			6132	2.3648	1.1421	7876	2.3621	1.1413
866	2.2907	—	8120	2.3954	1.1412	4-Nitro-3-phenylsydnone ‡		
1562	2.3055	1.1450	3-p-Chlorophenyl-4-phenylsydnone			313	2.2781	—
2027	2.3162	—	3069	2.3066	1.1435	720	2.2865	1.1446
2893	2.3345	1.1445	4730	2.3250	1.1427	1074	2.2938	1.1444
3623	2.3495	1.1445	7037	2.3501	1.1418	1465	2.3015	1.1443
5006	2.3787	1.1437	9117	2.3726	1.1408			

* This point was rejected because, although it is only slightly off the straight line, the least-square procedure overemphasises points at either end of the range of readings.

† This point was rejected because there appears to be curvature in the graph starting some way below this point. The other points are, however, on a good straight line.

‡ Measurements by Mr. P. G. Edgerley.

TABLE 2.

Compound	a	α	b	β	τP	ϵP	μ, D
3 : 4-Diphenylsydnone	2.2729	19.91	1.1448	-0.40	945.3	69.7	6.55
3-Phenyl-4- <i>p</i> -tolylsydnone	2.2728	19.63	1.1454	-0.29	996.2	74.5	6.72
4-Phenyl-3- <i>p</i> -tolylsydnone	2.2729	21.22	1.1455	-0.39	1063.9	74.5	6.96
3 : 4-Di- <i>p</i> -tolylsydnone	2.2727	21.21	1.1455	-0.34	1125.7	79.4	7.15
4- <i>p</i> -Chlorophenyl-3-phenylsydnone	2.2725	15.09	1.1454	-0.53	824.1	74.6	6.06
3- <i>p</i> -Chlorophenyl-4-phenylsydnone	2.2729	10.96	1.1448	-0.44	619.5	74.6	5.16
3 : 4-Di- <i>p</i> -chlorophenylsydnone ...	2.2724	7.93	1.1454	-0.54	513.4	79.5	4.61
4-Chloro-3- <i>p</i> -chlorophenylsydnone	2.2717	11.51	1.1456	-0.55	542.2	55.0	4.88
4-Nitro-3-phenylsydnone	2.2711	20.34	1.1448	-0.50	832.4	52.6	6.18

The errors in the dipole-moment values are estimated to be $\pm 0.02 D$.

DISCUSSION

In Part II (*J.*, 1949, 746), some progress towards complete elucidation of the molecular geometry was made by solving certain of the relevant vector triangles. Thus, from the electric dipole moments of 3-phenylsydnone itself, its 3-*p*-chlorophenyl and its 4-chloro- or -bromo-derivatives, and assumed values for the grouping $\text{Ph-N}_{(3)}$ and for the substitution moment of chlorine [taken as $\mu(\text{PhCl})$], the triangles ABC , ABC' , and ADB were solved as shown by Figs. 1, 2, and 3 of that paper; * *i.e.*, the relative directions of the moments of (a) 3-phenylsydnone (AB in Fig. 1), chlorobenzene (BC), and 3-*p*-chlorophenylsydnone (AC), (b) 3-phenylsydnone (AB in Fig. 2), the $\text{Ph-N}_{(3)}$ bond (BC'), and the sydnone ring itself (AC' , or μ_s), (c) 3-phenylsydnone (AB in Fig. 3), the halogenobenzene (DA), and the 4-halogeno-3-phenylsydnone (BD), could be ascribed in these three sets considered separately as the vector triangles ABC , ABC' , and ABD , respectively. The relation of the planes of the triangles ABC and ADB was, however, indeterminate; so it was possible only to say that the angle between the bonds $\text{Ph-N}_{(3)}$ and $\text{Hal-C}_{(4)}$ lay between the rather wide limits of 65° and 97° as shown by Figs. 4 and 5.

The plane of the triangle ABC' relative to ADB was likewise indeterminate, so the only statement which could be made about the direction of the $\text{Ph-N}_{(3)}$ vector (BC') was that it is at about 20° ($\pm 5^\circ$) to AC' . AC' was taken to be the moment of the sydnone ring itself; whence it was concluded that $\text{Ph-N}_{(3)}$ could actually be in the ring plane or up to 20° out of it (Fig. 6). This is not strictly true, because AC' (μ_s) is really the ring moment proper plus the vector due to the $\text{R}'\text{-C}_{(4)}$ moment which may not lie in the ring plane; so we do not necessarily know the orientation of $\text{Ph-N}_{(3)}$ relative to the atoms of the ring until and unless the orientation of the $\text{R}'\text{-C}_{(4)}$ bond thereto can be determined; though if the moment of $\text{R}'\text{-C}_{(4)}$ (which is either H-C or Ph-C) is small, this point is not important.

The problem, regarded as one in simple vector analysis, requires the evaluation of the three angles between three moment vectors which are not necessarily coplanar. Supposing, as was done in the previous paper, that there are no interaction moments to be evaluated in addition (see, *e.g.*, Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945), this requires three observations. These may be provided by measuring the three independent changes of moment which occur between the parent compound, its two isomeric monosubstituted derivatives, and its disubstituted derivative. The vector problem might therefore just be soluble; but even then the orientation of the ring plane cannot be related to the directions of the dipoles without making assumptions or adducing information external to the moment measurements. Therefore there is no prospect of a general, complete, and rigorous solution of the problem from dipole measurements alone; but at least it is an interesting exercise to see how far the enquiry can usefully be pushed.

The measurement of the moment of 4-chloro-3-*p*-chlorophenylsydnone permits the solution of a further triangle ACE (cf. Figs. D and E, where AC is again the moment of 3-*p*-chlorophenylsydnone, CE that of the $\text{C}_{(4)}\text{-Cl}$ bond, and AE that of the 4-chloro-3-*p*-chlorophenyl-compound). Furthermore, because both DA in Figs. 3, 4, and 5 and CE in Fig. D or E refer to the same bond ($\text{C}_{(4)}\text{-Hal}$),† it would appear possible to apply a test of

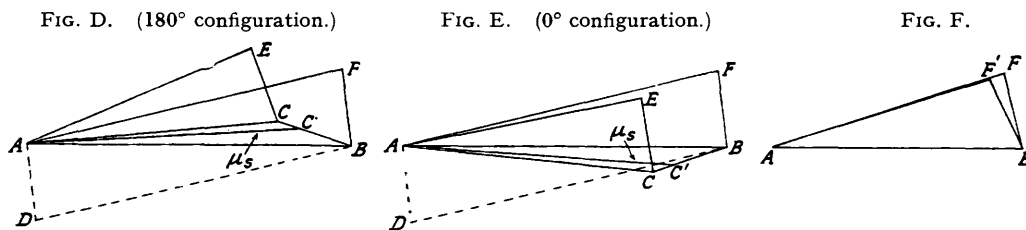
* Cf. footnote, p. 1483.

† The actual values in Figs. 3, 4, and 5 of Part II are for the bromo-compound. For the chloro-compound $\angle DAB$ is 83° .

consistency by adding triangle ACE to Figs. 4 and 5 and seeing which of these makes DA and CE more nearly parallel, as they must be from their physical significance.

For a reason which will appear later, in Figs. D and E, which incorporate Figs. 4 and 5 and show these relations, the vector triangle ABF is shown as an alternative, equivalent representation of the triangle ABD (broken line) which was used in the previous paper. From these figures it may be seen that consistency is obtained only if triangle ACE is joined, in the manner shown, to the 0° configuration, *i.e.*, to Fig. 5, when BF ($\equiv DA$) and CE prove to be parallel to within the limits of experimental error (see Fig. E), the angle between them being only 2.5° . With the 180° disposition of Fig. D, DA ($\equiv BF$) and CE are 15° out of parallel.

It therefore appears possible to obtain an essentially satisfactory solution of all the vector relations with the configuration shown in Fig. E. This requires that AC , BC , and BF ($\equiv DA$, or $\equiv CE$) be coplanar. It therefore requires also that BC' , BF , and AC' be coplanar, *i.e.*, that the $\text{Ph-N}_{(3)}$ bond, the substitution moment along the $\text{C}_{(4)}$ -Hal bond, and all the rest of the 3-phenylsydnone moment beyond that due to the $\text{Ph-N}_{(3)}$ bond, shall be coplanar. Much the most probable explanation of this vectorial condition is that the ring is planar and that the $\text{Ph-N}_{(3)}$ and the $\text{C}_{(4)}$ -Hal bonds lie in this plane. These conclusions would obviously provide strong support for the hybrid monocyclic structure (II).



The series of compounds produced by *p*-chloro-substitution in 3:4-diphenylsydnone can be used in exactly the same way: AB now corresponds to the moment of 3:4-diphenylsydnone, BC , BF , and CE to that of chlorobenzene, AC to that of 3-*p*-chlorophenyl-4-phenylsydnone, AF ($\equiv DB$) to 4-*p*-chlorophenyl-3-phenylsydnone, and AE to 3:4-di-*p*-chlorophenylsydnone. Essentially the same result is obtained in that the 0° configuration for triangles ABC and ADB is required for BF ($\equiv DA$) and CE to be nearly parallel, the angle between them then being 2.5° .

From the similar series produced by *p*-methyl substitution a rather different result is obtained, because the moment of 4-phenyl-3-*p*-tolylsydnone (6.96) is equal within experimental error to the sum of the moments of the parent compound 3:4-diphenylsydnone (6.55) and of toluene (0.35–0.40); so there is no ambiguity of orientation of vector triangles to be resolved, and the whole sydnone moment is found to be collinear with the axis of the 3-phenyl group, a relation which must be accidental. This result indicates very directly that the $\text{Ph-N}_{(3)}$ bond is coplanar with the sydnone ring; but because the substitution moment due to the methyl group is so small, the value of this indication is uncertain.

From all three series it is possible to derive values for the angle between the $\text{Ph-N}_{(3)}$ and $\text{X-C}_{(4)}$ valencies: in the first two, because the vectors DA and CE are parallel within 3° in the 0° configurations for each, the valency angles from these should be definite within this limit; but from the corresponding 180° configurations they are indefinite within 11 – 15° . The third series gives a single definite value. These are all given in Table 3.

It is also possible to estimate the magnitude and direction of the π -electron moment. This may be done if it be assumed that, though the sydnone ring remains a regular pentagon, the valencies radiating from it may be distorted from the regular pentagonal axes, any such distortion of the $\text{Ph-N}_{(3)}$ and $\text{X-C}_{(4)}$ bonds being symmetrical; so that the bisector of the angle between these two bonds is at 54° to the $\text{N}_{(2)}\text{-O}_{(1)}$ bond in the ring. Having thus assumed a relation between two moment vectors (BC and BF or CE) and the ring

skeleton, the direction of μ_S (AC') is fixed relative to it. Since a rough evaluation of the σ -bond moment for the skeleton, relative to $N_{(2)}-O_{(1)}$, has been made in Part II, the magnitude being 1.3 D and the direction -68° , this vector may then be subtracted from μ_S to give the magnitude and direction of the π -electron moment. The results of such calculations also are tabulated below.

From this Table it will be remarked that for the first two series the 0° configurations, which were judged the better ones by the consistency test, give large though not impossible values for the intervalency angle between the $Ph-N_{(3)}$ and the $Hal-C_{(4)}$ or $Ph-C_{(4)}$ bonds; but they also give values for μ_π which, while agreeing fairly well in magnitude, disagree badly in direction with those calculated by a molecular-orbital procedure. The latter

TABLE 3.

Configuration	Magnitude of μ_π , D	Direction of μ_π relative to $N_{(2)}-O_{(1)}$	Intervalency angle
<i>3-Phenyl-4-H series, chlorine substitution (first series)</i>			
0°	4.65	-12°	98.5°
180°	5.0—5.15	$+5.5^\circ-13^\circ$	$55^\circ-67.5^\circ$
<i>3: 4-Diphenyl series, chlorine substitution (second series)</i>			
0°	4.5	-27°	89.5°
180°	4.9—5.0	$+1.5^\circ-7.5^\circ$	$31^\circ-42^\circ$
<i>3: 4-Diphenyl series, methyl substitution (third series)</i>			
Coincident	4.65	-9°	65°
<i>3-Phenyl-4-H series, chlorine substitution (modified first series)</i>			
Assumed coincident	4.85	-2°	$76^\circ-83.5^\circ$
<i>3: 4-Diphenyl series, chlorine substitution (modified second series)</i>			
Assumed coincident	4.7	-10.5°	$61^\circ-65^\circ$
<i>Computed values *</i>			
	5.6	$+6^\circ$	$72^\circ \dagger$

* From Orgel, Cottrell, Dick, and Sutton (*loc. cit.*). Note.—In that paper angles measured clockwise were denoted as positive; in the present paper the more usual convention is observed.

† For a regular pentagonal ring. Enlargement might be expected.

The value of $\mu(PhCl)$ used above is 1.55 D, being derived by recalculating the data reported by Davis, Bridge, and Svirbely (*J. Amer. Chem. Soc.*, 1943, **65**, 857). Everard and Sutton (*J.*, 1951, 2807) use 1.60, derived from Le Fèvre and Le Fèvre's data (*J.*, 1936, 1130). Having regard to the nature of the assumptions made, this difference is trivial for the above calculations.

direction is in qualitative agreement with the expectations from the "resonance" interpretation of the problem; so the discrepancy is disturbing. The 180° configurations give intervalency angles which are smaller than the minimum value to be expected (72°); but they give reasonably good agreement between the observed and the calculated π -electron moment vectors. The third series gives only one set of results, showing a somewhat small intervalency angle and only fair agreement between observed and calculated π -electron moment vectors.

These observations suggest that there are interaction moments, which cannot be ignored, between the chlorine atom substituted in the 3-phenyl group and the sydnone ring *para* to it. If these are such as to reduce numerically the apparent substitution moments by chlorine, the difference between the results for the 0° and 180° configurations in each series is less, and will vanish if the substitution moment becomes equal to the numerical difference between the moments of the parent compound and the 3-*p*-chloro-derivative, *i.e.*, equal to 1.47 and 1.40 respectively for the first and second series, corresponding to interaction moments of 0.08 and 0.15 D, respectively. Then, as indicated already in the third series, the $Ph-N_{(3)}$ bond would be collinear with the total sydnone moment. The results in this limit, for μ_π and the intervalency angles are also tabulated, being designated as from the modified first and second series of measurements.

Values from the second modified series and the third series agree quite well, though both give a value for the intervalency angle which is less than the likely minimum, and neither gives very good agreement with the calculated magnitude or direction of the

π -electron moment. The modified first series gives a quite probable mean value (80°) for the intervalency angle, and quite good values for the magnitude and direction of the π -electron moment. Thus, both sets of derivatives from 3:4-diphenylsydnone agree in giving rather anomalous results, whereas those from 3-phenylsydnone give reasonable ones. This may indicate yet another kind of interaction moment.

Because of these complications it is now clear that there is no hope of a rigorous solution, even of the vector problem, unless the interactions can be evaluated independently. This might be possible if they were due only to electrostatic induction; so it has been attempted by the standard procedure (see, *e.g.*, Hampson and Weissberger, *J.*, 1936, 393).

The moments induced in the *p*-chlorine atom of the 3-*p*-chlorophenyl group by the sydnone group moment, and induced in the sydnone group by the corresponding carbon-chlorine dipole are small, being 0.045 and 0.065 D, respectively. Moreover, they are opposed: so the net induced moment is only 0.02 D. Were the Ph-N₍₃₎ bond to be collinear with the sydnone moment (μ_s) as supposed above, the actual interaction moment would have to be 0.08 or 0.15 D (see p. 1488). Clearly, therefore, it is due to other causes—probably to mesomeric interaction. A parallel case is *p*-chloronitrobenzene, wherein a difference of 0.15 D is found between the observed* and the calculated moment. This is such as to correspond to a smaller moment of substitution of hydrogen by chlorine, *i.e.*, of 1.40 D. Here, also, the interaction moment to be expected from simple electrostatic induction is very small, being only 0.005 D and in the opposite direction to the observed one. The moment postulated for this interaction is therefore plausible; but it cannot be given a firm quantitative basis.

The second type of suspected interaction is not merely impossible to calculate, but is even difficult to understand qualitatively. The vector diagrams for the modified first series of moments and for either the modified second series or the third series show that $\angle ABF$ is greater in the former than in the latter—see Fig. F, where BF represents the PhCl vector for the first series and BF' that for the last two. The same would be true of two triangles ACE and ACE' . If the former series is normal, as is indicated by the reasonableness of the results (see above), there is therefore an interaction moment FF' (about 0.4 D) in both the 3:4-diphenylsydnone series when substitution is effected in the *para*-position of the 4-phenyl group, and this is the same whether the substituent group is chlorine or methyl. If, on the other hand, the last two series are normal, as their consistency indicates, then there must be an interaction moment $F'F$ in the first series when the 4-hydrogen atom is substituted by chlorine.

The former alternative moment FF' is in the right direction for one electrostatically induced by the main sydnone moment (along AB , which makes an angle of about -15° to -20° to the N₍₂₎-O₍₁₎ axis) in a *para*-substituent on the 4-phenyl group: but such a moment, and a larger one at that, should also be induced in a substituent directly on the C₍₄₎ atom, so electrostatic induction would probably *invert* F and F' . A mesomeric mechanism by which electrons are transferred from the *para*-substituent, irrespective of whether it is Cl or CH₃, towards the 3-phenyl group seems unlikely. A moment FF' in the direction shown is therefore difficult to explain.

An opposite moment, $F'F$, could be explained by the chlorine atom substituted directly on C₍₄₎ acting as an electron source which, by a plausible mesomeric process, increases the main sydnone moment. The interposition of a phenyl group should reduce this process in the 3:4-diphenylsydnone derivatives. The fact that 4-nitro-3-phenylsydnone has a moment of only 6.18 D, instead of the 7.19 D to be expected for the geometry of triangle ABF for the first (3-phenylsydnone) series, supports this view; because the nitro-group is more electrophilic than the chlorine atom. Were it correct, however, the reason why the value for $\angle ABF'$ is so small, and why therefore the results for the intervalency angle and for μ_π are anomalous, would still be to seek.

For the sake of completeness we may briefly consider the possibility that some of the variation of derived intervalency angle is due to the effect of solvent on the observed dipole

* Mr. M. F. Saxby (personal communication) finds a value of 2.61 D for this substance which has previously been measured with varying results; cf. Wesson's "Tables of Electric Dipole Moments," M.I.T. Press, 1948.

moments. Frank remarked (see Sutton and Hampson, *loc. cit.*) that if, in any one solvent the moment of the parent compound and the substitution moments are definite in magnitude and direction, implying that the solvent effect shall not disturb any geometric relations assumed between the moments and their atomic framework, then calculations of intervalency angles from the changes in moment caused by substitution are not affected by solvent. These conditions appear to be satisfied, at least to a first approximation, if one may judge from the results for the intervalency angle in diphenyl ether. From the measurements given by Sutton and Hampson (*loc. cit.*) for the *p*-bromo-derivatives, and those of Leonard and Sutton (*J. Amer. Chem. Soc.*, 1948, **70**, 1568) for the *p*-fluoro-derivatives, the best value for the intervalency angle Ph-O-Ph from solution measurements is $121^\circ \pm 4^\circ$ if atom polarisation is ignored, and $123.5^\circ \pm 7^\circ$ if it is allowed for as in the former paper. The vapour-phase measurements by Coop and Sutton (*J.*, 1938, 1869) * give $124^\circ \pm 5^\circ$ for this angle. There is also a value of $118^\circ \pm 3^\circ$ from electron-diffraction work (Maxwell, Hendricks, and Mosley, *J. Chem. Phys.*, 1935, **3**, 699). The present application is of the same type; so the anomalies are probably not due to this cause.

Although there emerges no comprehensive and exact explanation of all the dipole moment evidence, the following conclusions seem justified: (a) The Ph-N₍₃₎ valency in 3-phenylsydnone, by a fortunate chance, is very nearly collinear with the main sydnone moment; and it therefore lies within 5° or so of the plane of the sydnone ring. (b) The angle between the Ph-N₍₃₎ and the C₍₄₎-X valencies is probably not greater than 80° ; so the latter valency is itself not more than 10° out of the plane of the sydnone ring. (c) The magnitude of μ_π is about 4.8 D. (d) The direction of μ_π is roughly parallel to the N₍₂₎-O₍₁₎ bond. Because of the complexity of the arguments, clear limits of error cannot be ascribed.

The conclusions support the meso-ionic structure (II), and agree reasonably well with theoretical calculations based thereon.

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