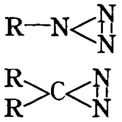
107. *Dipole Moments and Structures of the Organic Azides and Aliphatic Diazo-compounds.*

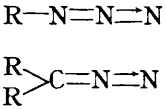
By Nevil V. Sidgwick, Leslie E. Sutton, and Wilfred Thomas.

Three types of formula are possible for the azides and aliphatic diazo-compounds :

(I.)



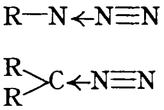
(II.)



$\mathrm{R{-}N{=}N\overset{\rightarrow}{=}N}$

$\mathrm{R_2{>}C{=}N\overset{\rightarrow}{=}N}$

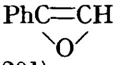
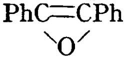
(III.)



$\mathrm{R{-}N{\leftarrow}N{\equiv}N}$

$\mathrm{R_2{>}C{\leftarrow}N{\equiv}N}$

The ring formulæ (I) were formerly accepted, but later work, especially that of Thiele, Angeli, and Staudinger, has led chemists to assume an open-chain structure, which in modern symbols must be expressed by (II) or (III).

The chemical evidence for the open chain is largely based on the fact that, if we assume a ring to be present, we must suppose that this breaks most easily at the single and not at the double link, both in reduction, and in addition reactions, such as the formation of pyrazole from diazomethane and acetylene, or of a 1 : 2 : 3-triazole from phenyl azide and acetoacetic ester, or of an aminoazo-compound from an azide and the Grignard reagent. The force of this argument is weakened by the fact that the double link between nitrogen atoms, unlike that between carbon atoms, is very strong, so that we might expect the single link to break first, as it does in the azo-compounds and in the aromatic diazo-compounds; this would not apply, however, to the behaviour on reduction, since hydrogen usually attacks the doubly-linked nitrogen atoms first, as in the reduction of azobenzene. The objection that a 3-membered ring with a double link involves too great a strain is weakened by the unexpected stability of the very similarly constituted acetylene oxides  and  described by Madelung and Oberwegner (*Annalen*, 1931, **490**, 201).

The physical evidence, so far as it goes, is in favour of the ring structures for these organic derivatives. Lindemann and Thiele (*Ber.*, 1928, **61**, 1529) and Lindemann, Wolter, and Groger (*ibid.*, 1930, **63**, 702) have shown that the parachors of the azides and the aliphatic diazo-compounds have the values to be expected for this structure, but the difference between the calculated values for the open-chain and the ring formulæ is only about 6 units. It was also pointed out (Sidgwick, J., 1929, 1108) that the boiling points of the azides and the aliphatic diazo-compounds lie very close to those of the corresponding bromides and chlorides respectively, and far below those of the nitro-compounds, which indicates that the dipole moments of these substances must be small, and therefore suggests that they cannot contain co-ordinate links.

For the azide ion, on the other hand, we have definite proof of an open-chain rectilinear formula from the crystal structures of the salts (Hendricks and Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 2904). This can be formulated in two ways, since a valency angle of 180° is compatible with either two double links or a single and a triple link : $[\mathrm{N}\overset{\leftarrow}{=}\mathrm{N}\overset{\rightarrow}{=}\mathrm{N}]^-$, $[\mathrm{N}{\leftarrow}\mathrm{N}{\equiv}\mathrm{N}]^-$. The first is, from its greater symmetry, much more probable.

It seemed likely that a knowledge of the dipole moments of these compounds would throw light on their structures, and we have therefore measured these moments for the phenyl, *p*-tolyl, and p-*chlorophenyl* derivatives of azoimide and diazomethane. The results obtained for the azides have been published (Sutton, *Nature*, 1931, **128**, 639), and values in satisfactory agreement with them for the phenyl and *p*-chlorophenyl azides, as well as for the *p*-bromo- and *p*-nitro-derivatives, are recorded by Bergmann and Schütz (*ibid.*, p. 1077 ; *Z. physikal. Chem.*, 1932, *B*, **19**, 389). We have also measured the moments of phenyl *iso*cyanate and its *p*-chloro-derivative, in order to obtain information as to the properties of a group which has a structure very like one of those suggested for the azides.

EXPERIMENTAL.

Preparation and Purification of Materials.—Benzene. A.R. Benzene was frozen out 4 times, dried, and distilled over Na.

Carbon tetrachloride. Messrs. Albright and Wilson's liquid for medicinal purposes was refluxed, and then distilled, over P_2O_5 in a stream of dry air.

Phenyl azide. This was prepared by Dimroth's method (*Ber.*, 1902, **35**, 1032) from NPhH·NH_2 purified as described by Fischer (*ibid.*, 1908, **41**, 73). The ethereal extract of the steam distillate was dried over $MgSO_4$, freed from solvent, and the residue distilled 3 times at 14—15 mm., the middle fraction being used; m. p. −27·5° to − 27·1°.

p-*Tolyl azide.* By the method of Dimroth and Pfister (*Ber.*, 1910, **43**, 2760), this was made from carefully purified *p*-toluidine; it was finally distilled twice in an oil-pump vac.; m. p. − 29·3° to − 29·0°.

p-*Chlorophenyl azide.* Similarly, this azide was made from carefully purified *p*-chloroaniline *via* *p*-chlorophenyldiazonium perbromide (Hantzsch, *Ber.*, 1895, **28**, 2756), and twice distilled in an oil-pump vac.; m. p. 19·9—20·1°.

Diphenyldiazomethane. This was prepared, after Staudinger, Anthes, and Pfenninger (*Ber.*, 1916, **49**, 1932), from benzophenonehydrazone, made from $COPh_2$ (m. p. 47—48°) as described by Curtius and Rauterberg (*J. pr. Chem.*, 1891, **44**, 194). After recrystn. from EtOH, the hydrazone melted at 97—98° (Curtius, 98°); it was oxidised in ligroin (b. p. $<$32°), the solvent removed, and the residue recrystallised from MeOH, the solutions being made up just above room temp. and cooled in a freezing mixture to cause crystn.; m. p. 30° (decomp.) (Staudinger, 29—30°). A better criterion of purity than the m. p. is the appearance of the substance: any ketazine shows up as a light film on the dark crystals of the diazo-compound. The specimens used gave concordant series of polarisations.

*Di-*p-*tolyldiazomethane.* This was prepared similarly (Staudinger and Goldstein, *Ber.*, 1916, **49**, 1924). The ditolyl ketone was prepared as described by Limpricht (*Annalen*, 1900, **312**, 92); m. p. after several recrystns. from MeOH 93° (lit., 92—95°). The hydrazone, after 3 recrystns. from EtOH melted at 108—109·5° (Staudinger and Goldstein, 108—110°); it was oxidised in C_6H_6, purified by fractional freezing, and then washed several times with MeOH, and recrystallised from hot MeOH; m. p. 102° (decomp.) (Staudinger and Goldstein, 101°).

pp′-*Dichlorodiphenyldiazomethane.* The requisite ketone was made according to Dittrich (*Annalen*, 1891, **264**, 175); m. p. 147° after 3 recrystns. from EtOH (Dittrich, 144—145°; Montagne, *Rec. trav. chim.*, 1902, **21**, 25, 147·75°); its hydrazone was made by heating the ketone in EtOH in a sealed tube with an equiv. of NH_2·NH_2,H_2O at 180° for 9 hr. The difficulties described by Staudinger and Goldstein (*loc. cit.*) in the case of the corresponding dibromo-compound were not met with; good yields of a pure substance were obtained; m. p. (from EtOH) 89·5—91·5°. This was shaken with an equiv. of yellow HgO in C_6H_6 for 12 hr., filtered, the solvent removed in vac., and the product recrystallised from ligroin (b. p. 60—80°), being cooled in a freezing mixture; m. p. 104° (decomp.).

Phenyl iso*cyanate.* This was distilled immediately before use in a stream of dry air directly into the weight pipette; b. p. 162°. It readily absorbs moisture with formation of crystals.

p-*Chlorophenyl* iso*cyanate* (Vittenet, *Bull. Soc. chim.*, 1899, **21**, 954). *p*-Chloroaniline was treated in dry C_6H_6 with a C_7H_8 solution of $COCl_2$, and the solution boiled for ¾ hr. till all the ppt. had dissolved. The *iso*cyanate had m. p. 29·5—30·5° after 2 recrystns. from ligroin in a freezing mixture (lit., 31°).

Measurement of Electrical Dipole Moments.—For the azides, these measurements were made in C_6H_6 solution by the methods and apparatus previously described (Sutton, *Proc. Roy. Soc.*, 1931, **133**, 668). On account of their instability, the diazo-compounds were measured in CCl_4 chloride solution at 0°, the rate of decomp. at this temp. being very slow; the dielectric consts. were measured in a cell of the Sayce–Briscoe type (see Ball, J., 1930, 570), which was immersed as far as possible in a well-stirred ice-bath. It was calibrated at 25° with pure C_6H_6; before the solutions were run in, a stream of dry air was passed through. The densities were measured in an apparatus designed to avoid errors due to the evolution of small bubbles of N, which precluded the use of a Sprengel–Ostwald pyknometer. It consisted of a pyknometer and an outer jacket; the former was an elongated bulb of about 10 c.c. capacity, with two capillary tubes sealed on axially; one of these ended in a fine jet, which could be covered by a ground-on cap, and had a small bulb blown near the middle; the other had a mark etched half way along it, and terminated in a small bulb from which another capillary, at right angles to the first, led to a small tap. The jacket was just long enough to contain the pyknometer, which fitted closely inside : it could be filled by a narrow external tube leading to the bottom.

The pyknometer was kept in the jacket, which was immersed in an ice-bath, for 45 min., to attain temp. equil. The jacket was then partially filled with the solution to be measured, which had also been cooled in the bath, and after a short interval the pyknometer was filled to the mark, the final adjustment being made by pressure on the rubber tube connecting it to a suction bottle, the tap closed, and the pyknometer withdrawn. It was immediately inverted and the bulb immersed in ice-water. The tap was then cautiously opened to allow some liquid to run into the bulb, and prevent the expansion or gas evolution from expelling liquid; the bulb in the tipped capillary (uppermost when inverted) broke the small column of liquid usually left in the tube, and so prevented it from being blown out.

Molecular Refractivities.—These could not be determined directly for the diphenyl or the ditolyl diazo-compound, because of the strong absorption in the visible region. The dichloro-compound, however, allowed some yellow light to pass, and determinations were made with this. It gave a refractivity 8·5 c.c. higher than that calc. from the obs. refractivities of other colourless or faintly coloured diazo-compounds (the average value for the CN_2 group being 7·9 c.c.; see Lindemann, Wolter, and Groger, *loc. cit.*), and it was concluded that this discrepancy was due to the absorption; so the refractivities used in calculating the dipole moments have been calculated from the above mean obs. value of 7·9 c.c.

The results are in the following tables, wherein f_2 is the molar fraction, d, ε, n the density, dielectric const., and refractive index for the Hg green line λ 5461. The densities are interpolated from a line through the exptl. values, that of pure C_6H_6 at 25° being taken as 0·8736. For CCl_4 at 0° and 25° the following values of the densities, dielectric const., refractive indices, and polarisations were experimentally determined :

	d.	*ε.*	P_1.	n_{5461}.	$_EP_1$.	n_{5790}.	$_EP_1$.
0°	1·6317	2·2768	28·1476	—	—	—	—
25°	1·5846	2·2263	28·1703	2·1329	26·6041	2·1276	26·5137

Phenyl azide in benzene at 25°.

f_2.	*d.*	*ε.*	*n.*	P_2.	$_EP_2$.
0·05357	0·8869	2·4697	1·50591	84·77	35·46
0·03633	0·8826	2·4075	1·50469	86·04	36·17
0·02454	0·8797	2·3644	1·50381	86·29	36·06
0·00945	0·8759	2·3081	—	85·99	—

P_2 at inf. diln. = 86·3; $_EP_2$ at inf. diln. = 36·15; $P_2 - {}_EP_2 = P_{A+O} = 50·15$;
$\mu = 1·55 \times 10^{-18}$ e.s.u.

p-*Chlorophenyl azide in benzene at* 25°.

f_2.	*d.*	*ε.*	*n.*	P_2.	$_EP_2$.
0·04974	0·8994	2·2975	1·50764	42·94	40·77
0·03362	0·8908	2·2901	1·50575	43·09	41·13
0·02318	0·8852	2·2857	1·50459	43·35	40·81
0·00923	0·8782	2·2794	—	43·64	—

P_2 at inf. diln. = 43·2 c.c.; $_EP_2$ at inf. diln. = 41·0 c.c.; $P_2 - {}_EP_2 = P_{A+O} = 2·2$ c.c.;
$\mu = 0·33 \times 10^{-18}$ e.s.u.

p-*Tolyl azide in benzene at* 25°.

f_2.	*d.*	*ε.*	*n.*	P_2.	$_EP_2$.
0·04757	0·8846	2·5347	—	115·1	—
0·03273	0·8811	2·4554	1·50436	116·9	41·0
0·02269	0·8786	2·4012	1·50355	117·9	40·19
0·00851	0·8753	2·3222	—	119·6	—

P_2 at inf. diln. = 120·3 c.c.; $_EP_2$ at inf. diln. = 41·0 c.c.; $P_2 - {}_EP_2 = P_{A+O} = 79·3$ c.c.;
$\mu = 1·96 \times 10^{-18}$ e.s.u.

Diphenyldiazomethane in carbon tetrachloride at 0°.

f_2.	*d.*	*ε.*	*n.*	P_2.	$_EP_2$.
0·03169	1·6065	2·3989	—	108·85	—
0·02134	1·6147	2·3578	—	107·6	—
0·01720	1·6180	2·3415	—	108·0	—
0·00766	1·6255	2·3052	—	106·8	—

P_2 at inf. diln. = 106·2 c.c.; $_EP_2$ (calc.) at inf. diln. = 61·0 c.c.; $P_2 - {}_EP_2 = P_{A+O} = 45·2$ c.c.;
$\mu = 1·42 \times 10^{-18}$ e.s.u.

Di-p-*tolyldiazomethane in carbon tetrachloride at* 0°.

f_2.	*d*.	ϵ.	*n*.	P_2.	$_EP_2$.
0·02322	1·6058	2·4206	—	155·0	—
0·02081	1·6085	2·4064	—	156·0	—
0·01634	1·6136	2·3794	—	156·6	—
0·01029	1·6203	2·3414	—	156·6	—

P_2 at inf. diln. = 157·4; $_EP_2$ (calc.) = 70·2 c.c.; $P_2 - {}_EP_2 = P_{A+O} = 87{\cdot}2$ c.c.; $\mu = 1{\cdot}96 \times 10^{-18}$ e.s.u.

Di-p-*chlorophenyldiazomethane in carbon tetrachloride at* 0°.
(Refractive indices measured at 25°.)

f_2.	$d^{0°}$.	ϵ.	P_2.	$d^{25°}$.	$n^{25°}_{5790}$.	$_EP_2$.
0·01715	1·6227	2·3046	82·5	—	—	—
0·01446	1·6241	2·2984	80·54	1·5759	1·4657	80·14
0·01209	—	—	—	1·5773	1·4647	80·52
0·00664	1·6282	2·2869	80·82	1·5807	1·4619	80·02
0·00605	—	—	—	1·5809	1·4617	80·89
0·00355	1·6298	2·2827	80·81	1·5825	1·4605	81·32

P_2 at inf. diln. = 81·0 c.c.; $_EP_2$ at inf. diln. : obs., 81·0; calc., 72·2 c.c; $P_2 - {}_EP_2$ (calc.) $= P_{A+O} = 8{\cdot}8$ c.c.; $\mu = 0{\cdot}62 \times 10^{-18}$ e.s.u.

Phenyl iso*cyanate in carbon tetrachloride at* 25°.

f_2.	$d^{25°}$.	ϵ.	$n^{25°}_{5461}$.	P_2.	$_EP_2$.
0·05951	1·5515	2·6200	1·4662	131·2	34·8
0·04142	1·5617	2·4995	1·4645	133·2	34·7
0·02781	1·5693	2·4083	1·4638	134·3	35·8
0·03940	1·5623	2·4886	1·4641	134·5	34·6
0·02932	1·5681	2·4187	1·4633	134·3	34·7
0·01973	1·5736	2·3555	1·4622	135·5	34·3

P_2 at inf. diln. = 137·5 c.c.; $_EP_2$ at inf. diln. = 34·5 c.c.; $P_2 - {}_EP_2 = P_{A+O} = 103{\cdot}0$ c.c.; $\mu = 2{\cdot}23 \times 10^{-18}$ e.s.u.

p-*Chlorophenyl* iso*cyanate in carbon tetrachloride at* 25°.

0·01622	1·5776	2·2442	—	53·8	—
0·01118	1·5798	2·2388	—	54·1	—
0·00747	1·5814	2·2347	—	54·1	—

P_2 at inf. diln. = 54·0 c.c.; $_EP_2$, calc. = 39·35; $P_2 - {}_EP_2 = P_{A+O} = 14{\cdot}65$ c.c.; $\mu = 0{\cdot}84 \times 10^{-18}$ e.s.u.

For the last compound the electron polarisation was calculated from the value obtained for phenyl *iso*cyanate, by adding 5·6 c.c. to allow for the replacement of hydrogen by chlorine.

DISCUSSION OF RESULTS.

The values found for the moments are given below; the azides were measured in benzene solution at 25°, and the diazo-compounds at 0°, and the *iso*cyanates at 25° in carbon tetrachloride. The results of Bergmann and Schütz (B.; *loc. cit.*) and of Eide and Hassel (E.; *Tidsskr. Kjemi Berg.*, 1930, **10**, 93) are added.

Dipole moments × 10^{18}.

R =	C_6H_5.	*p*-C_6H_4Me.	*p*-C_6H_4Cl.	*p*-C_6H_4Br.	*p*-$C_6H_4{\cdot}NO_2$.
$R{\cdot}N_3$	1·55	1·96	0·33	—	—
	1·55 (B.)	—	0·47 (B.)	0·64 (B.)	2·96 (B.)
R_2CN_2	1·42	1·94	0·62	—	—
$R{\cdot}NCO$	2·23	—	0·82	—	—
	2·34 (E.)	—	—	—	—

In every case the tolyl compound has a larger and the *p*-chlorophenyl compound a smaller moment than the phenyl compound, showing that the negative end of the dipole in the last is directed away from the benzene nucleus. With the azides the moment is very nearly the algebraic difference of those of the monosubstitution products. The moment of toluene is + 0·41 (Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 425) and that of *p*-chlorobenzene —1·56 (Bergmann, Engel, and Sandor, *ibid.*, 1930, *B*, **10**, 106). Assuming the moments to be collinear, we should have :

p-Tolyl azide : — 1·55 — 0·41 = — 1·96; obs. 1·96
p-Chlorophenyl azide : — 1·55 + 1·56 = 0·01; obs. 0·33.

The latter value corresponds to an apparent P_{A+O} of only 2·2 c.c., and it is quite possible that this is wholly atom polarisation P_A,* so that P_O and μ are really zero, and the moment of the C—N_3 group is collinear with the C—Cl moment and hence with the C—N covalency. If, however, it is a real moment, it shows that the inclination of the azide group moment to the C—N covalency is not more than 12°. It was previously argued (Sutton, *loc. cit.*) that this fact favoured the ring structure (I) in preference to either (II) or (III), but Bergmann and Schütz (*loc. cit.*) disagree. From the approximate agreement of the observed moments of *p*-chloro-, *p*-bromo-, and *p*-methyl-phenyl *iso*thiocyanate with those calculated, assuming simple additivity, from that of phenyl *iso*thiocyanate (Bergmann and Tschudnowsky, *Z. physikal. Chem.*, 1932, *B*, **17**, 101), they conclude that the double and single bonds of the nitrogen atom are collinear, and hence that the analogous open-chain structure Ph—N=N⇉N for the azides is not excluded. We have found similar approximate additivity of the group moments in *p*-chlorophenyl *iso*cyanate (μ obs. = 0·82; calc. = − 2·23 + 1·56 = − 0·67). Bergmann and Schütz's first conclusion is, however, disproved by their observation that carbodianil Ph—N=C=N—Ph and its *pp'*-dimethyl derivative have finite moments of 1·89 and 1·96. The obvious cause of the asymmetry is this. Each Ph—N link will lie in a plane perpendicular to that containing the N=C double link; the two spiran N=C links are themselves in perpendicular planes; hence the Ph—N links will lie in planes passing through the N=C=N axis and perpendicular to one another. Their moments will thus have components perpendicular to this axis and to one another, and so the molecule will have a finite moment. Incidentally, the magnitude of each component must be $1{\cdot}89/\sqrt{2} = 1{\cdot}34$, and this is the minimum value of the Ph—N= moment: the negative pole is nearer to the N atom (Hammick, New, Sidgwick, and Sutton, J., 1930, 1876). The approximate collinearity of the *iso*cyanate or the *iso*thiocyanate moment and the C—N valency must therefore be due to the inclined moments of the N=C=O or the N=C=S group not being large enough to give a resultant with the Ph—N moment which is notably inclined to the latter. The moment of the azide group must be subject to the same limitation; if we assume the above calculated minimum value for the Ph—N= link to hold in phenyl azide, and take the maximum possible angle of inclination of the total moment to the Ph—N link, 12°, the maximum moment for the N_3 group is 0·37, with the positive pole nearer to the benzene ring.

Of the three possible structures for the azide group, (II) is ruled out, because the N=N⇉N group by analogy with all other known co-ordinated compounds † would be most unlikely to have a moment so small as 0·4, and there is no probability of any mutual polarisation of the links reducing the total moment: it would rather increase it. (III) is impossible because the large moment of the co-ordinate link would cause the resultant of the whole molecule to be in the opposite direction to that observed. Similar objections apply to the open-chain formulæ (II) and (III) ‡ for the aliphatic diazo-compounds. Only the ring structures (I), could be expected to have moments of the observed magnitude and direction: in the azide the moment would be approximately that of the Ph—N< link, which, if the above calculated minimum value be accepted for this link, is not less than 1·3; in the aliphatic diazo-compounds it would be approximately that of two C—N links inclined at 48° 40′ (for valency distances, see Sidgwick and Bowen, *Ann. Reports*, 1931, **28**, 384), and if these are each taken to be about 1·0 [H_3C—N is about 1·2 (Hammick, New, and Sutton, J., 1932, 745), of which 0·2 may be due to the H_3C group (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 689)] the resultant is 1·82; this might be reduced by as much as 0·41 (the moment of toluene) by the moments in the Ph—C links, giving roughly the observed value.

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* Although an atom polarisation of 2 c.c. would change a moment of 0·3 to zero, yet it only changes one of 1·960 (as for *p*-tolyl azide) to 1·935.

† Examples are the bivalent carbon compounds; the *N*-ethers of the oximes; the sulphoxides and sulphones; and especially the co-ordination compounds of the halides of beryllium, aluminium, and boron with ethers, ketones, amines, nitro-compounds, etc., which have moments of 6—9 units (Ulich and Nespital, *Z. angew. Chem.*, 1931, **44**, 750; Nespital, *Z. physikal. Chem.*, 1932, *B*, **16**, 153).

‡ (III) is the only formula which would account for the optical activity of the diazo-compounds. This activity has, however, been shown not to be real (see Weissberger and Haase, *Ber.*, 1931, **64**, 2896; Weissberger and Bach, *ibid.*, 1932, **65**, 265; Ray, *J. Amer. Chem. Soc.*, 1932, **54**, 4753).

It has been suggested that since the linear azide ion, like the chloride ion, has no turning moment, it might be expected when it forms a covalency to produce the same moment as chlorine, so that the observed moment of the azide would be no argument against the linear structure. But if the structure is examined, it will be seen that this is not so, as was pointed out by T. C. Sutton (*Nature*, 1931, **128**, 872). When the chlorine ion forms a covalency, the only element of dissymmetry introduced is that caused by the shared pair of electrons. The symmetry of the azide ion, on the other hand, is due to the balancing of the two co-ordinate links against one another. If this symmetry were to be maintained when the ion becomes covalently linked, the new link would have to be formed by the central nitrogen atom. But this atom has no unshared electrons: the link can only be formed by one of the terminal nitrogen atoms, and this must destroy the symmetry and give a molecule with a large moment and a small stability, which presumably then goes over into the more stable ring form.

It would therefore seem that if the azides and the aliphatic diazo-compounds have any one of the three types of formula suggested above, it must be the first: they must be ring compounds. If they are tautomeric mixtures of any two, the amount of the open-chain form must be small, since its moment would be large; also the proportions must be much the same in the phenyl, tolyl, and chlorophenyl derivatives. It should be observed that, although the moments of molecules with formulæ (II) and (III) are in opposite directions, a tautomeric mixture of these two forms will not show a smaller moment; the molecules will orient themselves as individuals in the field, and the polarisation observed will be independent of the direction of the moment relative to the benzene ring. There is, however, one possibility left open. Pauling has suggested (*J. Amer. Chem. Soc.*, 1932, **54**, 988) that when two tautomeric structures have nearly the same energy content, a molecule may exist in a state of continuous and very rapid oscillation between the two. An oscillation of this kind, since it occurs in a time much less than that (about 10^{-7} second in solution) required for the orientation of the polar molecules in the field employed, must be supposed to give a moment which is the algebraic mean of those of the two structures. If we assume the azides (and a similar argument applies to the diazo-compounds) to consist of the two forms $\mathrm{R{-}N{=}N\overset{\rightarrow}{-}N}$ and $\mathrm{R{-}N{\leftarrow}N{\equiv}N}$ oscillating in this way, then, since the two predominant moments, those of the co-ordinate links, are equal and opposite, they should cancel one another (if the two forms are equally favoured), and we should be left with the small moment of the C—N link.

[*Note, added Feb. 1st, 1933.*] The measurement of the heats of combustion of phenyl azide and ethyl azidoacetate by Roth and Müller (*Ber.*, 1929, **62**, 1190) enables us to find the heat of formation from its atoms (H_a) of the azide group, and to compare it with those calculated for the rival structures; the results are somewhat remarkable. The value for the N—N link can be got from H_a for phenyl- or phenylmethyl-hydrazine, together with that for aniline or methyl-aniline, subtracting the value (87·0 kg.-cals.) for N—H in the amines (N—H in NH_3 is 89·8); that of N═N can be obtained in the same way from azobenzene. Using the fundamental values given by Bowen and Sidgwick (*loc. cit.*, p. 401) and the heats of combustion quoted by Kharasch (*Bur. Stand. J. Res.*, 1929, **2**, 359), and allowing for the heats of evaporation and, when necessary, of fusion, we obtain the following results (in kg.-cals. per g.-mol.) for the heats of formation of the links in the gaseous state from their atoms:

N—N: from $NHPh{\cdot}NH_2$, 34·3; from $NMePh{\cdot}NH_2$, 37·0; mean, 35·7
N═N: from azobenzene 86·8
N≡N: from gaseous nitrogen 208·0

From the value for C≡N in the nitriles (187·5) and in the *iso*cyanides (183·0), and from that of C≡O in carbon monoxide (quoted below), it seems that H_a is much the same for a co-ordinated link as for an ordinary covalency. We can therefore calculate what should be the value of H_a for each of the possible azide structures:

(I.) 2(N—N) + (N═N) = 71·4 + 86·8 = 158·2
(II.) 2(N═N) = 173·6
(III.) (N—N) + (N≡N) = 35·7 + 208·0 = 243·7

Roth and Müller's values give for the azide group N_3 from phenyl azide 205·9 and from ethyl azidoacetate 211·9, mean 208·9; this is almost exactly the mean of (II) and (III) (208·7). This seems to support the view that the azides have the two linear structures (II) and (III) in a state of resonance; although the difference of energy of the two states (70 kg.-cals. or 3 electron-volts) is rather large to permit of such resonance. It should be noticed that any strain in the ring structure (I) would diminish H_a (the strain in *cyclo*propane is above 20 kg.-cals.).

The values obtained for the multiple N—N links are in striking contrast to those given by C—C. In the latter the familiar strain which causes the instability of unsaturated compounds appears in the fact that the heat of formation increases less rapidly than in proportion to the number of links. As was shown before (*Ann. Reports*, 1931, **28**, 387), this is not true of the multiple links of carbon to nitrogen, oxygen, or sulphur, in which the increase is proportional to the multiplicity, or slightly greater. Since there must be some strain on the side of the carbon, this suggests that the multiple N—N and O—O links should show a negative strain, that H_a should increase more rapidly than the multiplicity. The figures given above show that this is true for nitrogen. That it also holds with oxygen can be deduced from the heat of conversion of hydrogen peroxide into water and oxygen. According to Matheson and Maass (*J. Amer. Chem. Soc.*, 1929, **51**, 674) the reaction $2H_2O_2$ (liq.) $\longrightarrow$ $2H_2O$ (liq.) + O_2 evolves 47 kg.-cals. The heat of evaporation of H_2O_2 at 20° can scarcely exceed that of water by more than 3 kg.-cals., which would give $2H_2O_2$ (gas) $\longrightarrow$ $2H_2O$ (gas) + O_2 + 41·0 kg.-cals. Whether we write H_2O_2 as H—O—O—H or as ${}^{H}_{H}\!>O\rightarrow O$, this reaction only involves the conversion of two O—O links into one O=O, so that we have $2(O{-}O) = (O{=}O) + 41$ kg.-cals., or $H_a(O{-}O) = \frac{1}{2}[H_a\,(O{=}O) - 41] = \frac{1}{2}(118 - 41) = 38{\cdot}5$ kg.-cals.

The relative values of the heats of formation of these links are thus (the C≡O value is taken from carbon monoxide):

C—C 1	N—N 1	O—O 1	C—N 1	C—O 1	C—S 1
C=C 1·8	N=N 2·4	O=O 3·1	C=N 2·0	C=O 2·3	C=S 2·2
C≡C 2·3	N≡N 5·8	—	C≡N 3·4	C≡O 3·3	—

This difference between the behaviour of carbon and that of the succeeding elements is presumably due to the presence of unshared electrons in the valency groups of the latter.

It thus appears that the dipole moments are compatible only with either the ring structure or resonance between the two linear structures; whilst the heat data are incompatible with the ring structure and give a value intermediate between the two linear structures, which themselves differ by an amount (3 volts) surprisingly large for resonance to occur.

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